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PHASE EQUILIBRIA IN POLY-COMPONENT GAS-LIQUID HYDROCARBON SYSTEMS

Preliminary Experiments on Complex Natural Systems and Studies on Selected Whole Turner Valley Mixtures.

by

T. W. Boyer, B. Sc.

Edmonton, Alberta. April, 1941.

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A THESIS

PHASE EQUILIBRIA IN POLY-COMPONENT GAS-LIQUID HYDROCARBON SYSTEMS

Preliminary experiments on Complex Natural Systems and Studies on Selected Whole Turner Valley Mixtures.

I. The precipitation of fractions from a Wainwright crude oil by modification of a light solvent with dissolved natural gas.

II. The equilibrium phase compositions in systems of a composite Turner Valley crude oil and Viking natural gas.

III. The Pressure-Volume-Temperature relations in natural gases over the temperature range 25°C to 98°C, and the pressure range 0 to 200 atmos.

and

Apparatus, methods and preliminary experiments in the study of the behavior of the gas-liquid system composed of the whole product of a Turner Valley oil well.

University of Alberta,	By- T.W.Boyer,B.Sc.
Department of Chemistry,	Under the direction
April, 1941.	of- Dr. E.H.Boomer.

PHASE EQUILIBRIA IN POLY-COMPONENT GAS-LIQUID HYDROCARBON SYSTEMS

Submitted in Partial Fulfil~~l~~ment
of the
Requirements for the Degree of
Master of Science

by

Thomas William Boyer, B.Sc.
Under the Direction of
Dr. E. H. Boomer.

Time devoted to this Work- 17 Months.

Edmonton, Alberta. April,1941.

1941
#1

UNIVERSITY OF ALBERTA

FACULTY OF ARTS AND SCIENCES

This is to certify that the undersigned have read and recommended to the Committee on Graduate Studies for acceptance, a thesis by T.W.Boyer,B.Sc. entitled-

PHASE EQUILIBRIA IN POLY-COMPONENT
GAS-LIQUID HYDROCARBON SYSTEMS

Professor
Professor
Professor

CONTENTS

Page

General Introduction........................ 1

Part I

Introduction................................ 4
Literature.................................. 8
Theoretical................................. 11
Materials................................... 15
Apparatus................................... 18
Procedure................................... 20
Results and Discussion...................... 21
Summary..................................... 26

Part II

Introduction................................ 27
Results and Discussion...................... 28
Summary..................................... 35

Part III

Introduction................................ 37
Literature.................................. 41
Theoretical................................. 45

Experimental

Materials.......................... 49
Apparatus.......................... 53
Procedure.......................... 64

Results and Discussion........................

P-V-T Relationships................ 72
Equilibrium Measurements........... 89
Table of Symbols................... 88
Summary..................................... 97
Appendix I.................................. 98
Bibliography................................104
Acknowledgement

GENERAL INTRODUCTION

The investigation of liquid-gas hydrocarbon systems has been receiving considerable and growing attention in recent years. Measurements of phase compositions and density on both simple two-component systems and the more complex systems found naturally in oil and gas wells or in the processing operations common to oil refineries have become quite extensive. Reference to the literature, as reviewed later in this thesis shows that little such work was in progress as recently as ten years ago but currently, several major investigations are under way. The information obtained is of use in correlating the behavior of individuals in the pure state with their behavior in complex-mixtures. Formally, the information gives values for the differential coefficients in the thermodynamic equations of state and it is hoped, rules leading to the prediction of the magnitude of the coefficients. In industry, the data is of value in serving as a guide to the proper conditions for satisfactory operation of oil fields and processes concerned with mixtures of hydrocarbons.

These investigations may be roughly divided into two types, namely, those concerned with the pressure-volume-temperature behavior of single phases of fixed composition, and those concerned with the properties and composition of two or more phases in equilibrium as a function of temperature and pressure. The present work is concerned with both types.

The investigations reported in this thesis are of two kinds. There is first a study of the effects of dissolved natural gas over a range of pressures and temperatures on the behavior of an initial single liquid phase of petroleum. Given sufficient gas in solution, the environment within the liquid phase may change to such an extent that a second liquid phase appears containing those compounds farthest removed in chemical and physical properties from the natural gas employed. The second part of this report is concerned with the equilibrium between two phases produced by contacting a light petroleum and natural gas over a range of pressures. The properties of the gas phase and the liquid phase in equilibrium and their relation to the properties of the original materials are determined and discussed.

In addition,as necessary information in the consideration of the above work, the behavior of the gas over a range of P-V-T was determined.

This work is an extention of other related work being carried forward in this laboratory under the general title "Phase Equilibria in Hydrocarbon Systems". Previous work has been concerned with relatively simple two-component systems and polycomponent systems of low critical pressures and temperatures. The investigations reported here represent a preliminary examination of the highly complex systems of relatively high critical pressures and temperatures comparable to petroleum natural gas systems found in nature.

This thesis will be presented in three sections.

Part I

The precipitation of fractions from crude oil by the modification of a light solvent with dissolved natural gas.

Part II

The equilibrium phase composition in systems of a composite Turner Valley crude oil and Viking natural gas.

Part III

The equilibrium phase composition in systems of a particular Turner Valley crude oil and natural gas. The P-V-T behavior of natural gas.

Part I.

PHASE EQUILIBRIA IN POLY-COMPONENT GAS-LIQUID HYDROCARBON SYSTEMS

The precipitation of fractions from a Wainwright crude oil by modification of a light solvent with dissolved natural gas.

INTRODUCTION

Currently, there are a number of different methods for bringing about a separation of petroleum into its components in the laboratory or the plant. The most common practice consists essentially of a careful fractional distillation at atmospheric and reduced pressures. In addition the use of selective solvents for the separation of particular fractions is practiced, particularly with regard to the preparation of lubricating oils. Frequently as a further aid to analysis, reactions such as nitration of aromatic compounds are taken advantage of to remove particular classes of compounds.

Excepting only in the case of the solvent method of obtaining fractions of petroleum, the methods of separation involve some chemical alteration in the materials treated. There are compounds in petroleum which readily undergo chemical changes even in the most careful process of fractionation. This is especially apparent in carrying out separation of the less volatile components as occur in the lubricating oil and asphaltic portions of petroleum. Further, it is not generally possible to use a chemical reaction to remove completely a class of components without at the same time effecting reaction to some extent with other components. In contrast to these processes, selective extraction of petroleum by suitable solvents offersa method of fractionation free from any chemical reactions.

The commercial application of solvent refining processes in the recovery of lubricating oil fractions is of recent origin and phenomenal growth. A variety of solvents, sulphur dioxide, furfuraldehyde, phenol, nitrobenzene, chlorinated hydrocarbons, glacial acetic acid and propane (2) have been used. They may act to extract preferentially the desired paraffinic hydrocarbons or conversely the undesired naphthenes, resins and asphalts. In either event the desired product is obtained in a quality superior to that obtained from distillation processes.

Fractional precipitation, by the modification of a light solvent through the solution of natural gas, is a process analagous to solvent extraction. There are numerous patented processes in the petroleum refining industry using solvent extraction methods in which the solvent may be modified by addition of other substances. For instance, the solvent from one stage in an extraction process is used, plus its dissolved material, as the extracting solvent at a later stage. The extraction of kerosene with alcohol followed by the use of this solution as the extracting agent for a petroleum residue is an example (5).

These processes are not without some disadvantages. Excepting propane, the solvents are not products of petroleum itself, or even closely related to petroleum. Some are toxic, others, e.g. sulphur dioxide, are corrosive in the presence of water

and some are unstable and are subject to oxidation. They all present a problem in their recovery for further use. Except in the case of propane, sulphur dioxide and a few other low boiling solvents, the process of recovering the solvent usually requires a fractional distillation with its attendant problem of thermal decomposition of the product. Since in most cases one hundred per cent recovery of the solvent is impossible this loss may make the cost of the process prohibitive. Finally, while the extent of removal of a fraction by the solvent is controllable through the extent of extraction, most solvents are highly specific and remove only one class of components. A complete process requires the use of a number of solvents to effect a complete fractionation of the oil.

The principle object of this investigation was to achieve the fractionation of crude oil by varying the nature of the solvent through the addition of methane under pressure to the solution. The liquid solvents used were petroleum fractions and the source of gas was Viking natural gas. This gas was used directly and may be considered substantially methane.

The process offers attractive possibilities as an analytical method useful in obtaining those fractions which are readily decomposed by heat. The ease of control of the solvent properties obtained by adjusting the pressure of the gas should permit the production of a series of fractions of any desired degree of closeness. Its commercial applications, especially

in the field of petroleum refining cannot be discussed without more investigation. Further investigation may be warranted because the solvent and gas are byproducts of the refining process, and up until recently, the latter has found no application in the industry except as fuel.

All these facts coupled with the fact that the gaseous solvent can be entirely removed under exceedingly mild conditions of temperature using simple apparatus, appear to offer for this solvent process a range of applicability offered by no other solvent. By the choice of a sufficiently low boiling liquid solvent, decomposition attendant to its removal may be eliminated. The process may be entirely physical and presents only the disadvantages of requiring special equipment to withstand the high pressures.

LITERATURE

The literature on the subject of this work is relatively scanty.

As previously stated the use of preferential solvents in the separation of heavy oils and tars has been an established practice in the manufacture of lubricants for some time. However the use of a dissolved gas as a means of control of solvent properties has received little attention.

S. von Pilat and M. Goldewicz (2), appear to be the initial workers in applying the principles involved to the refining of petroleum or petroleum fractions. They used the residues of a crude oil from Polish fields dissolved in propane or ethane. The solvent properties of the propane were modified by the solution of methane under successively higher pressures. They obtained a succession of precipitated fractions. The heavier and less soluble constituents precipitated first and were followed by the precipitation of lighter and more soluble fractions at higher pressures. At one hundred and thirty atmospheres all but a small fraction of the crude oil, consisting of light oils, had precipitated out. All of the fractions were liquid and easily separated.

Further investigations using solutions of the crude in propane were carried out, and even extended to solutions of the crude oil and methane alone under high pressure.

S. von Pilat in another paper (2), suggests a possible process for a fractional precipitation on an industrial scale. He suggests the arrangement of saturation vessels, pumps, expansion chambers, etc but gives no data or probable operating conditions.

M.R. Taylor (2), fractionated Alberta Bitumen, from the MacMurray Tar Sand area, under high pressure. A forty per cent solution of the Bitumen in gasoline yielded a precipitate which was not analysed.

E.S. Hillman and B. Barnett (2) have published meager information on a method for the analysis of heavy residual oils, involving a fractional precipitation from a gaseous solution. The oil is first dissolved in isopentane and the isopentane soluble fraction is dissolved in propane. The addition of successive increments of methane to the propane solution yields successive fractions. They used the internal pressure as a measure of the solvent power. Methane having the lowest internal pressure of the paraffin hydrocarbons decreases the internal pressure of the solution thus reducing its solvent power, resulting in the precipitatioh of the least soluble fractions. They confined their studies to asphalts and petroleum residues and give no description of technique etc, only the results of its application.

Robert W. Henry and James V. Montgomery obtained a patent (10) for a process involving the modification of propane as a

solvent by adding methane to decrease the relative solubility of the dissolved material in the solution.

THEORY

The work is not new in so far as the fundamental conceptions are concerned but only in its applications. It is based upon the developments in solvent extraction by propane in particular, and the pioneering work of Pilat and Goldewicz (2) on the modification of solvent properties by dissolved natural gas.

The broad principle "like dissolves like" of the alchemists is at the background of all extraction processes, and while the theory of solutions has progressed greatly since the time of alchemy, the principle is still a reliable qualitative guide. Thus, an ideal solution is one which obeys Raoult's law, is an arbitrary and useful definition based on experiment. Upon examination of such solutions it is found that in general the molecular species are very much alike. On the other hand solutions which deviate widely from Raoult's law may show partial or complete immiscibility or at least a maximum or minimum in the boiling point diagram. In such cases the components show marked differences in properties and molecular structure.

The theory of solutions due to Hildebrande (2) based upon the concept of internal pressures serves as a useful guide of some quantitative value. The resultant of the Van der Waal's forces, repulsive forces and thermal pressure gives the internal pressure. This pressure in liquids is very large and parallels directly the degree of development of dipoles in the molecules of the liquid. Thus we can say that liquids of similar inter-

nal pressure or liquids made of molecules of similar electrical structure, will be miscible; and the degree of miscibility will vary more or less as the similarity between the molecular structure of the components becomes less.

One would predict that two components as similar in molecular structure as n-pentane and n-hexane, would obey Raoult's law and be completely miscible. This would also be true of solutions of benzene and toluene. However, it would not be expected that two substances like propane and a paraffin wax would obey Raoult's law or even be miscible at low temperatures. The lack of similarity in molecular construction and the large difference in internal pressure, that for propane being small, about one thousand atmospheres and that for wax being high, about three thousand atmospheres accounts for the lack of ideality in the solutions. Again, while benzene and n-pentane are miscible in all proportions under ordinary conditions, the solutions do not obey Raoult's law and show a minimum on the boiling point diagram. When a sufficiently complex aromatic liquid is chosen of much higher internal pressure than benzene, the deviation from Raoult's law in solutions with pentane becomes evident in the phenomenon of partial miscibility.

Paraffins generally show small internal pressures, which increase with molecular weight and length of chain. The other hydrocarbon constituents of petroleum have greater internal pressures or more highly developed dipoles, that also increase

regularly with molecular size and length. The hydrocarbons containing other elements than carbon and hydrogen, such as oxygen, are the most different from the lower paraffins and should show the least solubility in the paraffins.

All the hydrocarbon series are represented in petroleum, as well as resins and asphalts in many cases. The proportions of each constituent and class of constituents vary over wide ranges for different petroleums. For a particular petroleum, which is a complex solution, the possibility exists of producing such a wide range of internal pressure by additions of suitable hydrocarbons that a separation into two layers may result. This can be done by adding compounds of high or low internal pressure. Thus with a highly asphaltic crude oil the addition of pentane, which has a relatively low internal pressure, may precipitate some of the asphalt, forming a two phase system. Using propane instead of pentane the effect will be more pronounced resulting in the precipitation of more asphalts and possibly some naphthenes or aromatics. This is the principle of solvent refining of lubricants by propane. The addition of methane is the final step possible. It has the lowest internal pressure of the paraffin hydrocarbons and has no dipole moment. Methane, being a gas under ordinary conditions, requires the application of pressure to make it go into solution in petroleum. In the relation between the pressure and solubility of methane in liquids lies the means of exact and easy control of the quantity dissolved and hence of the range of internal pres-

sures within the liquid. The introduction of methane into petroleum in increasing amounts may be expected to precipitate the heavy hydrocarbons in order of their decreasing internal pressure. Theoretically other gases than hydrocarbons would be expected to give similar results, but practically, it is doubtful.

In practice, the use of methane in modifying internal pressures in a crude oil has definite limitations. In the case of light oils the solubility is high, but at high methane concentrations in the gas phase, the transfer of volatile components to the gaseous phase is quite large (2). Methane is most soluble in the volatile components and as they are transferred to the gas phase the proportionality between gas solubility and pressure no longer holds. In fact the increase in solubility for increments of pressure becomes quite small. Considering a particular two component system such as benzene and methane at 25°C and 430 atm. (2) the system is single phase, that is the benzene and methane have become miscible in all proportions. In order to maintain a liquid phase it is necessary to add an excess of the liquid and limit the gas phase. As a result, a separation into two liquid layers may not be obtained under any conditions. Oils of a heavy nature having low volatility also present difficulties. In these oils the solubility of the methane is relatively small even at high pressures. Generally, a volatile liquid solvent must be added in order to provide a suitable medium for the solution of methane.

MATERIALS

Natural gas from the Viking field as supplied by the City of Edmonton was used in this work. On analysis (8) it was found to consist of:

CH_4	90.97%
C_2H_6	2.41
C_3H_8	0.58
C_4H_{10} & up	0.34
N_2	5.70
S	6 to 8 grains/100 cu.ft.

The gas contains traces of sulphur, added as an oderant, which has no appreciable effect on the physical behavior of the gas.

Ligroin, Eastman Practical, was employed as the volatile solvent serving as a diluent for the crude petroleums used. Its properties are presented in Table I - 1. It consists largely of volatile paraffin hydrocarbons.

Table I - 1

Properties of Ligroin

Density $\frac{20^\circ}{4^\circ}$	0.706
Solubility Conc. H_2SO_4	2.0%

A.S.T.M. Distillation

I.B. Pt.	68°C	60%	79°C
10%	76	70	80
20	77	80	81.5
30	77.5	90	83.5
40	78	97	87
50	78.5	LOSS	3%

Two petroleums were used in this work. Through the courtesy of Imperial Oil Limited, a composite sample of Turner Valley petroleum was obtained from the Calgary terminus of the Royalite Oil Company pipeline from the field. This petroleum is a high grade, mixed base type with paraffinic properties. The properties of this petroleum are presented in Tables I - 2 and I - 3.

Table I - 2

Properties of Turner Valley Petroleum

Density $\frac{20}{4}$ 0.8077

A.S.T.M. Distillation at 701 mm. Hg

I.B. Pt	25.0°C
5%	73.0
10	89.0
20	124.0
30	153.0
40	188.0
50	236.0
60	277.0
70	328.0 (Cracking started)

The second petroleum used was a heavy, black, viscous, asphalt base crude oil from Battleview Oils Limited, in the Wainwright field. Its Properties are presented in Table I - 4.

Table I - 3

PROPERTIES OF FRACTIONS OF TURNER VALLEY CRUDE .

Cut No.	%	Cut Temp. °C	Press.	$d\frac{20^\circ}{4^\circ}$	Refractive index	$\frac{20^\circ}{0^\circ}$
Gas	2.18					
1	8.61	57.4	701mm	0.6309	1.3503	
2	14.99	93.2		0.7055	1.3960	
3	21.85	114.4		0.7427	1.4160	
4	28.29	137.0		0.7613	1.4272	
5	35.38	165.8		0.7777	1.4372	
6	41.48	185.4		0.7882	1.4420	
7	50.07	225.0		0.8037	1.4490	
8	53.96	148.4	40	0.8238	1.4596	
9	57.78	157.0		0.8344	1.4664	
10	61.56	174.8		0.8406	1.4703	
11	65.48	188.0		0.8424	1.4698	
12	68.98	200.0		0.8482	1.4725	
13	72.97	182.2	10	0.8650	1.4818	
14	76.53	200.0		0.8764	1.4896	
15	80.51	180.8	1	0.8766	1.4888	
16	84.51	193.6		0.8829	1.4919 ✓	
17	88.50	215.6		0.8913	1.4980 ✓	
18	92.49	251.3		0.9046	1.5064 ✓	
19	100.00	Residue		0.9385	----	

✓ Extrapolation of refractive index of kerosene solutions to zero concentration.

Table I - 4

Properties of Wainwright Petroleum

Water	2.55%
Sediment	0.3 %
Density $\frac{20}{4}$ (dry)	.9647

A.S.T.M. (Petroleum as Received)

I.B. Pt.	98°C (Water)
2.5%	165°C (First oil drop)
5	203
10	265
20	294 (Cracking started)

A.S.T.M. (Dehydrated Petroleum)

Cracking started before distillation.

The Turner Valley Petroleum was washed with alkali to remove the corrosive sulphur compounds. Some of the experiments were carried out on Turner Valley Petroleum topped to 200°C. Further runs were performed on the crude oil, dewaxed at -29°C and topped to 200°C.

The Wainwright petroleum was dehydrated at 110°C until all foaming ceased. No attempt was made to remove the trace of sediment. In one case, the distillate up to 150°C removed from the Turner Valley petroleum, was used as a solvent for the Wainwright petroleum. Generally, ligroin was used as solvent for this oil.

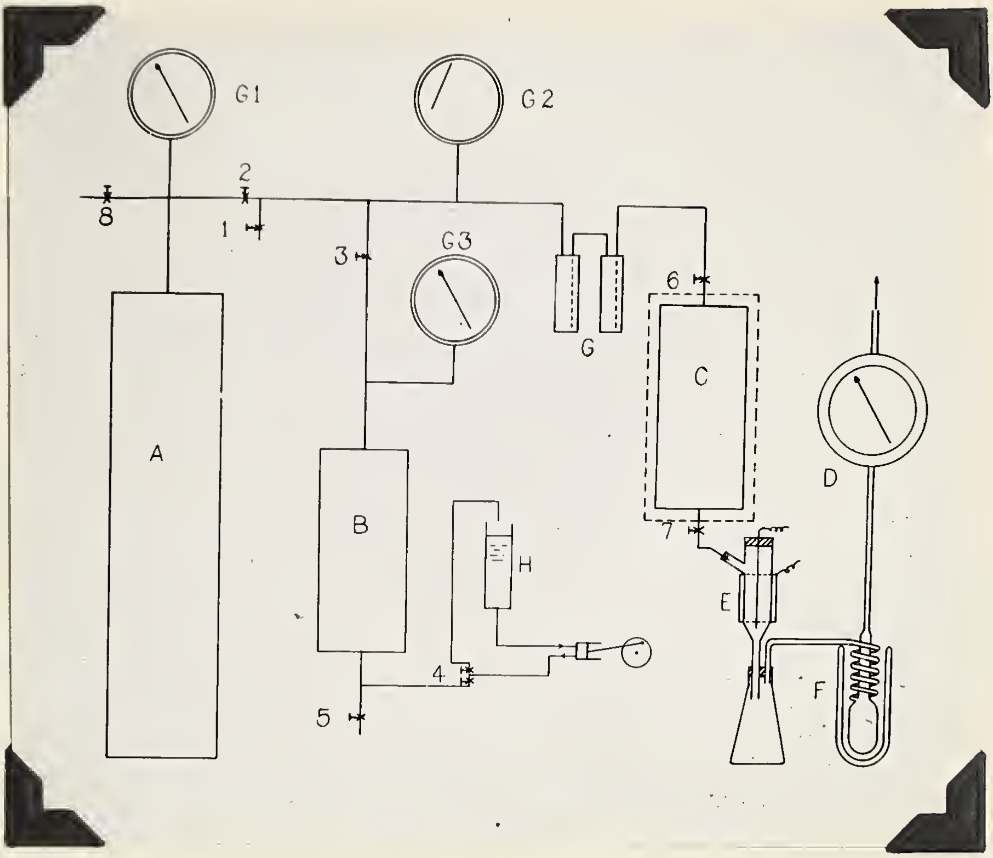


Figure I-1.

Diagramatic representation of the compressor, storage and equilibrium cylinder system.

APPARATUS

The apparatus consisted of a gas compression and storage system and the equilibrium chamber as shown schematically in Figures I - 1 and I - 2.

Compression and Storage of Gases

Viking natural gas was compressed in a three stage compressor, the intake of which was fitted directly to the City gas mains. The gas was pumped into a fifteen litre storage cylinder A (Fig I - 1) through valve 8. Pressures up to four thousand p.s.i. could be obtained with this compressor. Pressures up to five thousand p.s.i. were obtained by means of a hydraulic pump with a capacity of one quart per hour. A fifty per cent glycerin-water solution used, acted as a fluid piston in the cylinder B. Starting with the system filled by gas at four thousand p.s.i., any pressure up to five thousand p.s.i. could be obtained by pumping the fluid into cylinder B with valve 2 closed. Pressures in the system were given by Bourdon tube gauges calibrated by reference to a standard, dead weight, piston gauge.

The Equilibrium Cylinder

The equilibrium cylinder is shown schematically in Fig. I-2 It is a stainless steel cylinder of 5 litre capacity. Valve

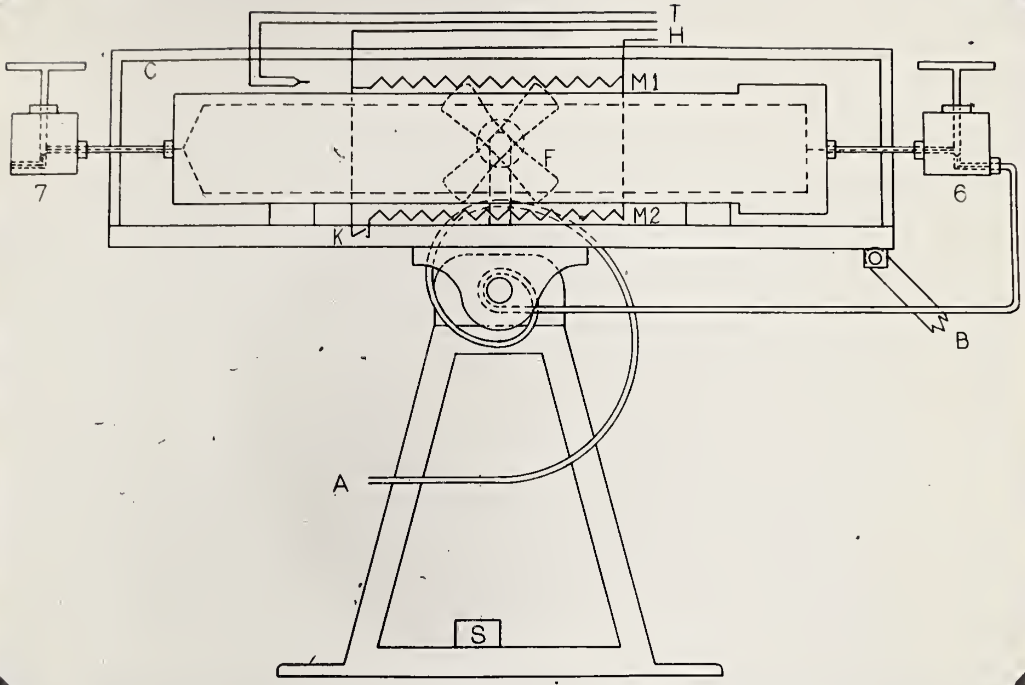


Figure I-2

Details of the equilibrium chamber.

6 on one end of the cylinder controlled the admission of gas, the valve 7 on the other end was used for charging and discharging oil. Preliminary experiments with a 3 litre cylinder proved unsatisfactory due to the small size of samples obtained.

The cylinder was mounted as illustrated and oscillated by means of a crank arm on a slow speed reduction gear driven by a half horsepower electric motor. An air bath made of an asbestos-lined wooden box covered the equilibrium cylinder assembly. The temperature in this air bath was controlled thermostatically. The air in the air bath was circulated by a small fan driven from the rocker motor. An electric heater placed opposite the fan was connected to an on-off relay which was controlled by a potentiometric recording controller connected at H. An iron-constantan thermocouple was connected to the controller at T. It was found thatthis assembly could maintain the temperature in the air bath to ± 2.5°C. Due to its large heat capacity, the temperature of the cylinder, as obtained from insulated surface thermocouples, varied by only ± 0.1°C. For temperatures above 25°C an auxilliary heater M_2 was fixed in the box below the fan. This heater could be turned on or off at will by a knife switch K on the side of the base board. This heater was used only for the initial heating of the air bath and cylinder. At the higher temperatures the electrical circuit of the main heater was arranged so that the controller cut in and out an external resistance. Thus, the heater was

always on but the amount of heat produced changed according to the sign of the temperature variations from the set point.

The discharging apparatus shown in Fig. I - 1 consisted of a Cottrell electrostatic precipitator E, a condenser F and a wet test gas meter D. The Cottrell precipitator was found necessary to catch the fog of atomized oil produced by the evolution of the dissolved gas upon expansion to atmospheric pressure. The precipitator was operated by a 24 watt Cox coil operating on a six volt accumulator. The condensor was submerged in an ice salt mixture in a Dewar flask. The exit from the condensor led to the gas meter.

Softening Point Apparatus

To obtain a qualitative measure of the changing properties of the precipitated asphalt layers, a ball and ring apparatus made to A.S.T.M. specifications was used (2). The tests were conducted according to A.S.T.M. specifications.

Experimental Procedure

The experimental procedure used has been reported in detail along with the analytical procedure by Davis (2).

RESULTS AND DISCUSSION

All tests made on Turner Valley Petroleum were unsuccessful in that no noticeable separation into two phases occured. The same negative result was found when using the residue from Turner Valley petroleum topped to 150°C and to 200°C. Tests made at elevated temperatures 50°C, 75°C and 100°C using the crude oil topped to 200°C and pressures up to 5000 p.s.i. likewise produced negative results. Further runs were performed on solutions of the oil topped to 200°C in ligroin, using first, 50% by weight of ligroin and second, 60% ligroin. Again results showed no separation of a second liquid phase. A final attempt using the crude oil, dewaxed at -29°C and topped to 200°C dissolved in twice its weight of ligroin and under a pressure of 5000 p.s.i. produced no separation into two layers or precipitate of any kind.

The reason for these negative results evidently lies in the fact that Turner Valley petroleum contains a high percentage of paraffins, relatively small amounts of aromatics and naphthenes, and no asphalts (2). The internal pressure of the solution must be decreased relatively, very greatly, in order to reach a point at which the aromatics and naphthenes would precipitate out. Evidently, the solubility of methane in the system of crude oil alone or of crude oil plus ligroin, was not sufficient to produce the required range of internal pressures for a separation. It is possible that in place of ligroin, materials of lower

internal pressure such as propane and butane would produce the desired result. Tests using propane or butane were not carried out as they would have necessitated a complete remodeling of the apparatus to handle these liquified gases. The possibilities which the use of propane or butane solutions suggest, seem to warrant some experimental investigation and there is every reason to believe that the results would be more promising.

The first attempts on the Wainwright oil at 25°C and 75°C using no solvent and pressures up to 3800 p.s.i. produced negative results. The next two attempts using solutions of the Wainwright oil in the distillate up to 150°C overhead temperature from the Turner Valley crude oil, both failed to show any separation. Solutions of forty per cent and fifty per cent crude oil were used.

A solution of 64.5% by weight of ligroin and 35.5% by weight Wainwright crude oil when charged into the cylinder was found to separate into two layers on the addition of natural gas. Solutions of this composition were used in all further experiments. In runs 19, 20, 22, and 26 a fractional precipitation was induced by using successive pressure increments of 500 p.s.i. from approximately 1500 to 3500 p.s.i. gauge pressure (2). The experimental data derived from the analysis of the fractions obtained is presented in Table I-5.

This table gives the weight per cent, density in grams per

Table I - 5

UPPER AND LOWER LAYERS FROM WAINWRIGHT CRUDE OIL AFTER REMOVAL OF SOLVENTS

Pressure, lbs per sq. in.	Run No.	1595	2120	2634	3120	3660
Upper Layer: weight %	19	94.0	91.3	89.2	87.9	87.0
	20	93.7	91.0	87.7	85.3	83.9
	22	92.6	89.1	85.8	82.8	84.0
	26	91.2	88.0	84.8	82.2	80.6
	average	92.9	90.2	87.4	84.8	82.4
Lower Layer: weight %	19	6.0	2.7	2.1	1.3	0.9
	20	6.3	2.7	3.3	2.4	1.4
	22	7.4	3.5	3.3	3.0	2.4
	26	8.8	3.2	3.5	2.3	1.6
	average	7.1	2.7	2.8	2.6	2.4
Softening Point °C	19	129	104	99	79	70
	20	109	103	87	69	54
	22	103	115	96	78	54
	26	104	115	102	78	53
	average	116	107	96	78	54
Density: gr/ccm	19	1.094	1.057	1.110	1.087	1.055
	20	1.099	1.083	1.073	1.059	1.050
	22	1.087	1.063	1.069	1.067	1.053
	26	1.095	1.087	1.075	1.059	1.050
	average	1.095	1.083	1.072	1.062	1.050

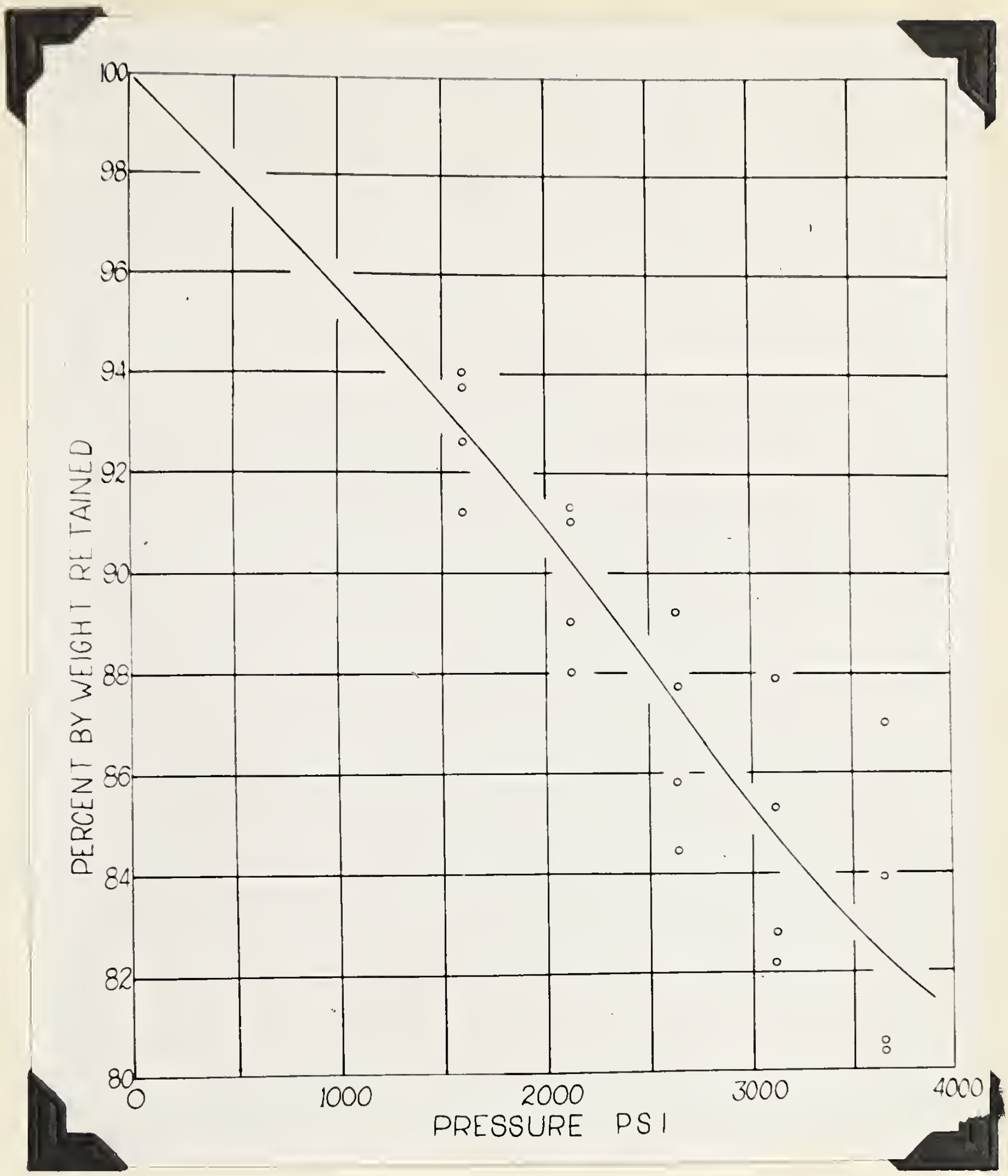
Run number	19	20	22	26	average
Final upper layer:					
Density, gr/ccm.	0.918	0.886	0.904	0.920	0.907
Cracking temp. °C	369	330	313	333	338

Note: "Average" values are read from the graphs of the data.

cubic centimeter, and the softening point in degrees centigrade of the precipitated layer for each pressure. In the discussion to follow the upper layer will be called the refined oil and the lower layer will be called precipitated oil.

From the tabled properties it can be seen that a true fractionation was obtained. The properties vary regularly with increasing gas pressure. This regular variation of the properties with pressure suggests that the materials precipited at the lowest pressures, i.e. with the least change in internal pressure, are those with the highest internal pressures and most unlike the natural gas added. These will include the carbenes, asphaltenes and asphalt resins. A complete Soxhlet extraction analysis, molecular weight determination and an ultimate analysis of the precipitated oil should have been done in order to characterize the material completely. In this preliminary investigation, time did not permit such a procedure. Further, in a continuation of this work, a lower initial pressure, say 500 p.s.i. and possibly higher pressures to 5000 p.s.i. should be used.

The results indicate, that in accordance with the assumption ~~that~~ equal increments in pressure of gas, i.e. in the solubility of the gas, produce proportional decreases in the internal pressures. The amount precipitated, for each increment in pressure of 500 p.s.i., is about 2.6% of the crude oil. Evidently, a complete series of compounds of differing internal pressures occurs in the oil.



Part I

Per cent of refined crude oil in the upper layer.

Table I - 6

A.S.T.M. DISTILLATION ON REFINED OIL

Run No.	19	20	22	26
Bar. Press. mm Hg	706	697	701	701
I.B.P.	114.5°C	112.0°C	107.0°C	113.0°C
10%	141.0	150.0	129.8	152.0
20	205.0	228.5	175.0	261.5
30	369.0 ✓	312.5 ✓	289.0 ✓	308.0 ✓
40		325.0	313.0	322.0
% Yield before cracking	32	41	42	45
Cracking temp. °C	369.0	330.0	313.0	333.5

✓ Slight coloration of distillate.

In Table I-6 the results of an A.S.T.M. distillation of the refined oil are listed. Whereas the original oil could not be distilled without cracking, over 40% of the refined oil could be distilled over without cracking. Moreover, up to 30% over, the distillate was water white. This is an important and unexpected result, that the removal of a relatively small percentage of heavy complex compounds, should increase the vapor pressure of the remaining constituents far enough to permit their removal by distillation without decomposition at atmospheric pressure. This result requires further investigation before an explanation can be offered.

The large discrepancies in the experimental data are probably due to a lack of standardization of procedure and to the inherent difficulties in handling the products. Refinements in the analytical procedures would have to be worked out and standardized before absolutely reproducable results could be obtained. A more suitable method of removing the two liquid layers separately and completely must be devised. The difficulty may be made apparent when it is realized that the precipitated oils are semi-solids at the lower pressures and very viscous liquids at the higher pressures.

These experiments, of an exploratory nature, show that the solubility of the heavy components, asphaltic in nature of Wainwright crude oil in a light hydrocarbon solvent may be controlled by the solution of methane under pressure. The

properties of the solvent may be easily and accurately controlled by the pressure of gas, to produce a series of precipitated fractions. The possibility of obtaining, in their naturally occuring state, by a simplified and accurate procedure, the heavy components of the oil, is indicated. Herein lies the possibility of an analytical method leading to fractionation of the crude oil without the possibility of thermal decomposition or chemical change. The possibility exists also that this process could be extended to the refining of crude oil on a commercial scale. The removal of a small percentage of the heavy complex compounds leaves a refined oil markedly different in its properties, and more amenable to processing when compared to the original crude oil.

SUMMARY

In this investigation, preliminary experiments on a method of analysis of crude oil, through fractional precipitation by the modification of a solvent by dissolved natural gas, were described. The results indicated that such a procedure is quite possible.

However the work with Turner Valley oil showed a limitation to the applicability of the method in its present form. This limitation may be removed through the use of a number of liquid solvents of differing internal pressure. Further work using propane or butane or both appears desireable.

A true fractionation of a selective nature of the crude oil into heavy and light fractions was obtained. The possibilities of the process as an analytical or refining procedure were indicated. It was suggested that further work of this nature is desireable.

Part II.

PHASE EQUILIBRIA IN POLY-COMPONENT GAS-LIQUID HYDROCARBON SYSTEMS

The equilibrium phase compositions in systems of a composite Turner Valley crude oil and Viking natural gas .

Part II

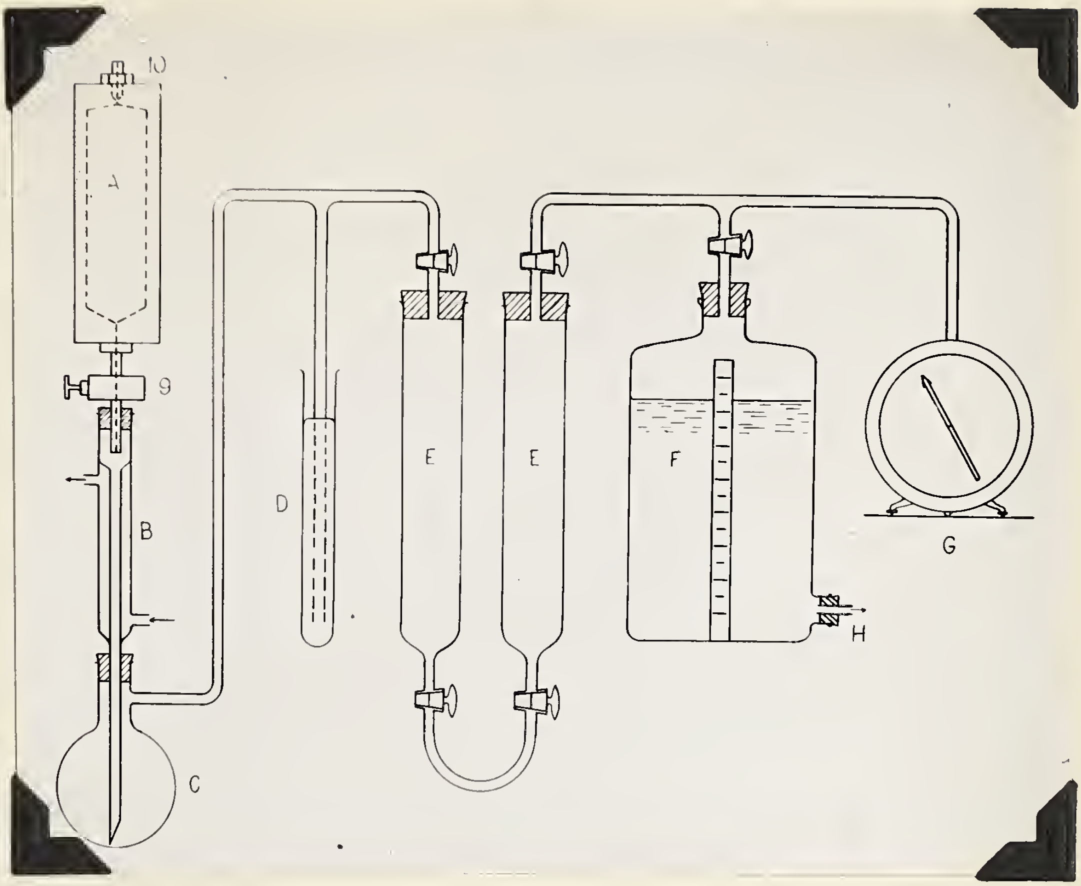
INTRODUCTION

Preliminary investigations, on the behavior of a crude oil-natural gas system under pressure, were performed. These investigations were carried out using a composite sample of Turner Valley crude oil (see Part I) and Viking natural gas.

The apparatus and the experimental and analytical procedures employed have been described in detail by Davis(2).

In this report it is intended only to indicate and discuss briefly the results obtained, and to indicate where improvements were found necessary in order to obtain the accuracy desired for further more precise investigations. A discussion of the underlying theory will appear in Part III.

The preparation of the oil samples is described in Part III The Viking natural gas used was taken directly from the supply mains and used without treatment for removal of sulphur or water vapour. It was found necessary to remove the sulphur from the oil by scrubbing with dilute sodium hydroxide solution in order to prevent corrosion of valve seats.



Part II.

Expansion Train.

Table 1

EXPERIMENTAL DATA

Expt. No.	1	2	3	4	5	6	7	8	9	10	11	12	13
Gauge Pressure p.s.i.	2634	2634	2634	2634	2634	2120	2120	1595	1595	1065	1065	510	510
Vol. oil chgs.(ccm)	1083	1083	1083	2167	2167	1083	2168	1083	2168	1083	2168	1083	2168
Wt. Oil chgd. (gms)	874.4	874.7	874.9	1750.2	1750.2	875.1	1750.7	875.1	1750.9	875.1	1750.8	875.1	1750.8
Vol. Gas $\frac{25^{\circ}}{760mm}$ (ccm)		986,900	994,300	829,600	811,100	809,800	662,400	628,300	391,700	393,400	341,500	191,800	170,300
Wt. Gas (gms)		690.2	705.5	588.6	575.5	574.6	470.0	445.8	277.9	279.1	242.3	136.1	120.8
Liquid Sample													
Wt. Oil (gms)	99.46	99.94	99.63	98.84	96.03	101.93	102.20	105.40	105.11	110.23	110.73	115.97	116.30
Wt. in Charcoal(gms)	4.11	4.65	4.76	4.99	5.06	5.22	4.80	5.00	4.60	3.89	2.57	2.76	2.85
Vol. Pentane (ccm)	3.0	2.5	2.5	3.0	3.1	3.0	2.9	2.8	1.7	2.2	1.2	1.7	1.7
Vol. Gas (ccm)	13,880	13,630	13,370	13,180	13,320	10,180	11,230	8720	8800	6090	6141	3040	2870
Wt. Gas (gms)	9.66	9.13	9.15	9.12	9.25	7.09	7.77	5.90	6.07	4.16	4.26	2.14	1.98
Gas Sample													
Wt. in charcoal(gm)		1.47	2.21	1.55	2.64	1.10	1.78	1.00	1.10	0.84	0.33	0.37	0.85
Vol. Pentane (ccm)	1.0	1.47	1.5	1.2	2.0	0.9	0.8	0.3	0.1	0.1	0.1	0.1	0.1
Vol. Gas (ccm)	38,090	36,430	35,490	34,390	34,210	28,890	28,660	21,400	20,800	13,000	13,810	5,810	5,830
Wt. Gas (gms)	26.70	25.54	26.13	25.48	23.83	20196	20.61	15.04	14.55	8.06	9.90	4.08	4.11

RESULTS AND DISCUSSION

The experimental conditions and extensive quantities for this investigation are presented in Table II-1. Pressures are gauge pressures and volumes are corrected to 25^{o}C and 760mm Hg. The data under "liquid sample" and "gas sample" are on the whole material taken from the sample pipettes. Two different quantities of oil were used at each pressure to give a rough idea as to the effect of the gas/oil ratio on the results. Special attention is drawn to the data for the pentane recovered from the charcoal. This quantity was only measured to 0.5 ccm, and consequently errors as high as 50 to 100% are possible. This is especially true for the gas phase at low pressures.

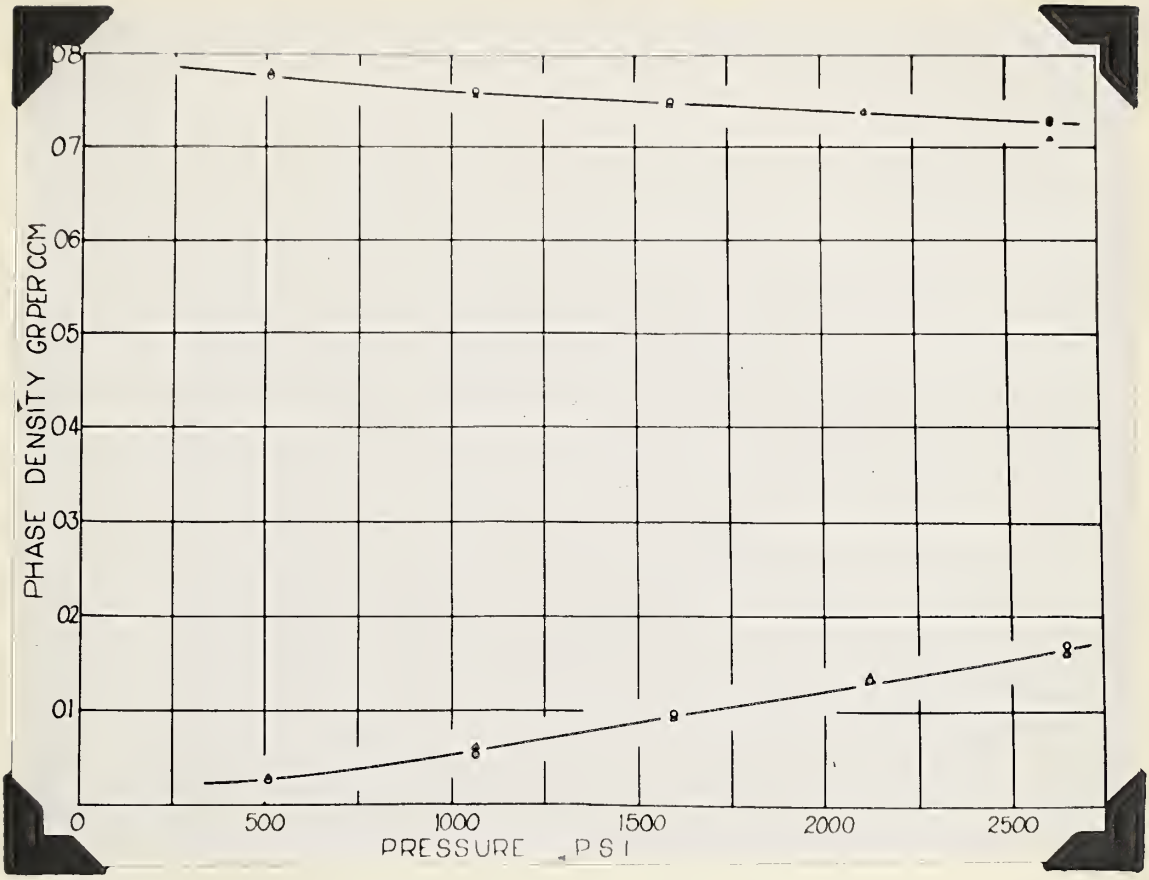
The experimental data in Table 1 were used to derive the specific properties of the system as tabled in Table II-2. The phase densities as calculated from the masses of the phase sample and the volumes of the sample pipettes are probably accurate to 0.2% for the liquid phase and 0.5% for the gas phase. The data for pentanes from runs 10 to 13 inclusive has little significance other than to indicate that there was a small amount of pentane in the gas phase.

The discrepancy between duplicate experiments is attributed to the inability to reproduce pressure readings to better than about 1%. This would account for the errors bearing in mind the effect on both phases.

Table No. II - 2

PROPERTIES OF THE PHASES IN EQUILIBRIUM

Exp. No.	1	2	3	4	5	6	7	8	9	10	11	12	13
Press. p.s.i.	2634	2634	2634	2634	2634	2120	2120	1595	1595	1065	1065	510	510
Vol.charge ccm	1083	1083	1083	2167	2167	1083	2168	1083	2168	1083	2168	1083	2168
Liq.Phase Dens. gms/ccm		0.7310	0.7299	0.7261	0.7089	0.7340	0.7378	0.7476	0.7443	0.7603	0.7557	0.7770	0.7787
Liq. Phase Spec. Vol - $\frac{1}{d}$		1.368	1.370	1.377	1.410	1.362	1.355	1.337	1.344	1.316	1.323	1.287	1.284
Gas Phase Dens. gm/ccm		0.161	0.169	0.161	0.1579	0.1316	0.1336	0.0957	0.0934	0.0531	0.0611	0.0266	0.0296
Gas Phase Spec. Vol $\frac{1}{d}$		6.203	5.916	6.199	6.333	7.573	7.480	10.449	10.72	18.83	16.37	37.59	33.78
Vol. Gas Phs.ccm.		3889	3914	2509	2435	3897	2641	3906	2799	3929	2759	4009	2879
Vol. Liq. " "		1284	1259	2664	2738	1276	2532	1267	2375	1244	2414	1164	2294
Gas Phs/Liq.Phs.		3.029	3.109	0.941	0.889	3.054	1.043	3.083	1.179	3.158	1.143	3.444	1.255
Comp. Gas Phase													
Butanes & lighter ccm		36700	36200	34840	34980	29140	29370	21850	21330	13430	13960	5980	6270
gms		26.07	27.40	26.28	25.22	21.40	21.89	15.85	15.49	8.84	10.17	4.39	4.90
Pentane & Heavier ccm		1.5	1.5	1.2	2.0	0.9	0.8	0.3	0.3	0.1	0.1	0.1-	0.1-
gms		0.94	0.94	0.75	1.25	0.56	0.50	0.19	0.16	0.06	0.06	0.06	0.06
Gas-oil ratio in Gas Phs.ccm/ccm		$2.45x10^4$	$2.41x10^4$	$2.90x10^4$	$1.75x10^4$	$3.23x10^4$	$3.66x10^4$	$7.27x10^4$	$8.51x10^4$	$13.39x10^4$	$13.95x10^4$	$5.97x10^4$	$6.23x10^4$
Comp. Liq. Phase													
Gas Recovered ccm		15260	15090	14910	15050	12040	12890	10520	10770	7490	7150	3990	3870
gms		12.21	12.24	12.23	12.37	10.43	10.75	9.15	9.61	6.67	6.08	3.84	3.77
Liquid Recovered ccm		124.5	124.5	124.0	122.1	128.0	127.9	132.8	131.2	138.2	137.7	144.7	145.2
gms		101.51	101.20	100.72	97.97	103.81	104.02	107.15	106.17	111.61	111.48	117.03	117.36
Gas-oil Ratio in Liq. Phs.ccm/ccm		$1.23x10^2$	$1.21x10^2$	$1.20x10^2$	$1.23x10^2$	$0.94x10^2$	$1.01x10^2$	$0.79x10^2$	$0.82x10^2$	$0.54x10^2$	$0.52x10^2$	$0.28x10^2$	$0.27x10^2$



Part II.

Phase Densities in the Equilibrium Cylinder.

Gas Phase/Liquid Phase 3.1:1 —— o ——

" " " " 1.1:1 —— Δ ——

Within the limit of experimental error the phase densities are the same for different gas/oil ratios. It can be predicted that the phase densities of the liquid and gas phases would both increase with increasing gas/oil ratio because of increasing transfer of the more volatile components to the gas phase. Beyond a certain gas/oil ratio however, the density of the liquid phase would remain practically constant while the gas phase density would decrease, approaching in the limit the density of Viking gas at the same pressure. The phase density curves slope slightly towards each other but do not suggest that a critical or consolute pressure at which the system becomes single phase can be reached. This is only to be expected on the further grounds that the oil contains appreciable quantities of material of very high boiling point.

Along with the decreasing density due to solution of gas there is a corresponding decrease in the viscosity (2) of the liquid phase. Consequently, in order to promote rapid and easy flow of oil through the porosities in a producing horizon, as much gas as possible should be retained in solution.

The most interesting results are those illustrating the transfer of the more volatile components from the liquid to the gas phase. Viking gas is free from all but traces of hydrocarbons higher than methane. However, at equilibrium the gas phase has a higher density than the Viking gas at the same pressure. This is illustrated by the following data on densities.

Pressure p.s.i.	510	1065	1595	2120	2634
Phase density	0.0275	0.0605	0.0950	0.128	0.161
Viking gas density	0.0264	0.0581	0.0918	0.1245	0.1547

The values for the density of Viking gas are from Johnson (12). This transfer of material to the gas phase is also shown directly in the pentane content of the gas. The pentane content shows a minimum about 1000 p.s.i., and shows an increasing concentration at higher and lower pressures. This result is to be expected and has been frequently demonstrated in more simple systems (12). At atmospheric pressure the vapor content of the gas phase will be high and dependent on the vapor pressure of the volatile constituents in the crude oil.

Since the materials used in this investigation are quite dissimilar from those found in say the Turner Valley field, in that the gas is deficient in heavier hydrocarbons and the oil is deficient in the more volatile components, these facts must be kept in mind when applying the results to a producing area. Since the presence of higher hydrocarbons in the gas phase promotes the transfer of material from the liquid phase to the gas phase, the pentane content found here is smaller than might be expected under comparable conditions in the field. Data on the Turner Valley field during its early stages of development are scanty and only approximate figures can be given with regard to the gas cap wells. It is probable that the well pressures were in the neighborhood of 2000 to 2500 p.s.i. and the naphtha content of the gas was 0.25 to 0.5 gallons per

1000 cu.ft. (2). This corresponds to a gas/oil ratio range of 24900 to 12460 ccm. of gas (at N.T.P.) per ccm. of naphtha. The temperatures in the producing horizons are not well known and may vary from 25°C (2) to 98°C (22). Comparing these figures with the experimental gas/oil ratios in Table II-2, the agreement is as good as can be expected. Currently the pressures in the naphtha region are much lower, being only 300 to 1000 p.s.i. and the gas/oil ratio is much higher, corresponding to approximately 1,000,000 ccm. of gas per ccm. of naphtha. Again this is in general agreement with the experimental results but suggests that equilibrium does not now exist in the naphtha producing areas in the field. Referring to Fig. II-1, it is seen that the ability of the gas to hold vapors decreases with increasing pressure to a minimum. The course of events in the producing horizon, as the pressure dropped, may be visualized as a progressive condensation of naphtha in the formation. Consequently the gas removed from the well contained less naphtha vapors. At sufficiently low pressures, below 1000 p.s.i., there should be increased yields of naphtha, but this has not been observed in continuously operated wells. Apparently contact between the remaining gas and naphtha is not of sufficiently long duration to reestablish equilibrium conditions. Generally, a decrease in gas/oil ratio is observed in shut-in wells, an observation that could be predicted as a result of an approach to equilibrium conditions.

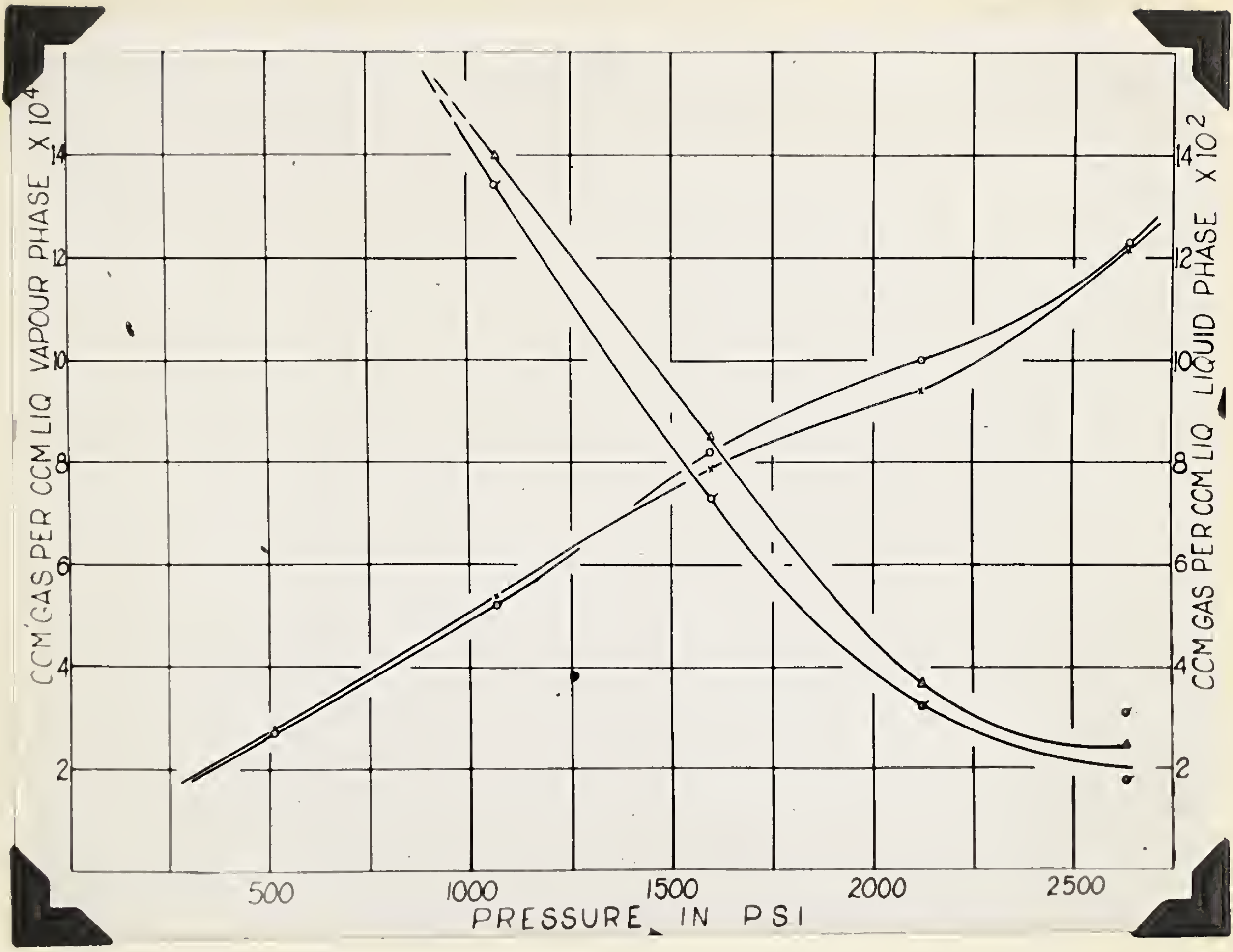


Figure II-1

Gas/oil Ratio in the Phase Sample.

Liquid phase oil over all gas/oil ratio 3:1 ——x——
" " " " " " " " 1:1 ——o——

Gas phase over all gas/oil ratio 3:1 ——√——
" " " " " " " 1:1 ——Δ——

The results of this investigation suggest that the original state of the materials in the naphtha producing formation was a gas phase. The fact that comparable gas/oil ratios are obtained in the laboratory using Turner Valley crude oil to saturate the gas suggests also that the production from the naphtha wells originates in a gas cap above the crude oil. In other words, there is a connection between the formations producing crude oil and those producing gas. The writer is not competent to discuss the geologic features that may confirm or disaffirm this view. The observed slow increase in pressure in shut in naphtha wells may be due to pressure equalization in the sands immediately adjacent to a well or, in the light of the above discussion, may be due in part to flow of gas from the oil sands to the naphtha sands.

In the application of these results to operations in the field, it is obvious that the highest recoveries of naphtha are obtained at the highest pressure. In short, pressure conservation should be practiced. In addition, the rate of the pressure drop should be kept at a minimum in order that the naphtha condensed in the formation during the pressure drop be given an opportunity to remain in equilibrium with the gas, thus the highest possible naphtha concentrations in the gas corresponding to the pressure are obtained. Operating a naphtha well at or even near its capacity is very poor practice from the point of view of ultimate recovery of the

naphtha. It should be practiced only if combined with a process of repressuring; the gas after being stripped of naphtha being returned to the formation in adjacent wells. Given sufficient data on the gas composition pressure and temperature, the time to reach equilibrium in the formation, and the economics involved, the most advantageous rate of gas flow in any area can be estimated. Such a procedure, while leading to the most economic recovery of naphtha, will, on the assumption that the gas phase is in connection with the crude oil phase, conserve pressure and gas so essential to the highest recovery of crude oil.

The data given in Table II - 2 with regard to the liquid phase are of interest principally in their relation to the behavior of the gas phase. The value of gas in solution underpressure in crude oil is generally admitted and conservation is generally practiced in so far as is economically feasible. The dissolved gas reduces the viscosity and density of the oil and upon liberation of the gas in the formation, provides the driving force necessary to lift the oil to the surface. The time during which the well will flow without the use of pumps and the ultimate recovery of oil is increased by gas conservation.

The solubility of natural gas in crude oil has been shown many times (2) to follow Henry's law up to moderate pressures with negative deviations at the higher pressures. This is

Table 3

FRACTIONAL DISTILLATION DATA ON OILS

Expt. No.	Original Crude Oil	1,2,3	4, 5	6	7	8	9	10	11	12	13
Pressure p.s.i.		2634	2634	2120	2120	1595	1595	1065	1065	510	510
Gas Phase/ Liq. Phase		3.067	0.965	3.054	1.043	3.083	1.179	3.158	1.143	3.444	1.255
2.5%	42.3°C	72.0	66.4	67.3	66.6	64.0	63.0	57.6	54.6	54.0	52.6
5.0%	58.4	84.7	82.8	82.8	82.0	77.0	79.5	77.0	71.1	69.7	69.0
7.5%	72.1	93.8	92.2	91.7	90.6	86.7	90.2	88.5	84.5	82.3	79.7
10.0%	83.4	104.0	100.0	99.1	99.0	96.4	99.7	98.8	94.0	93.1	88.8
12.5%	93.4	113.5	109.0	110.5	107.8	103.0	107.4	105.0	103.5	101.6	99.6
15.0%	102.9	123.0	116.0	118.4	115.0	113.3	114.8	113.0	110.0	109.2	108.4
20.0%	121.0	140.4	134.0	135.4	135.0	131.6	133.4	131.0	126.6	124.4	124.6
% over at 150°C	27.8	23.0	24.3	24.0	24.4	24.3	24.6	25.0	26.0	26.7	27.0

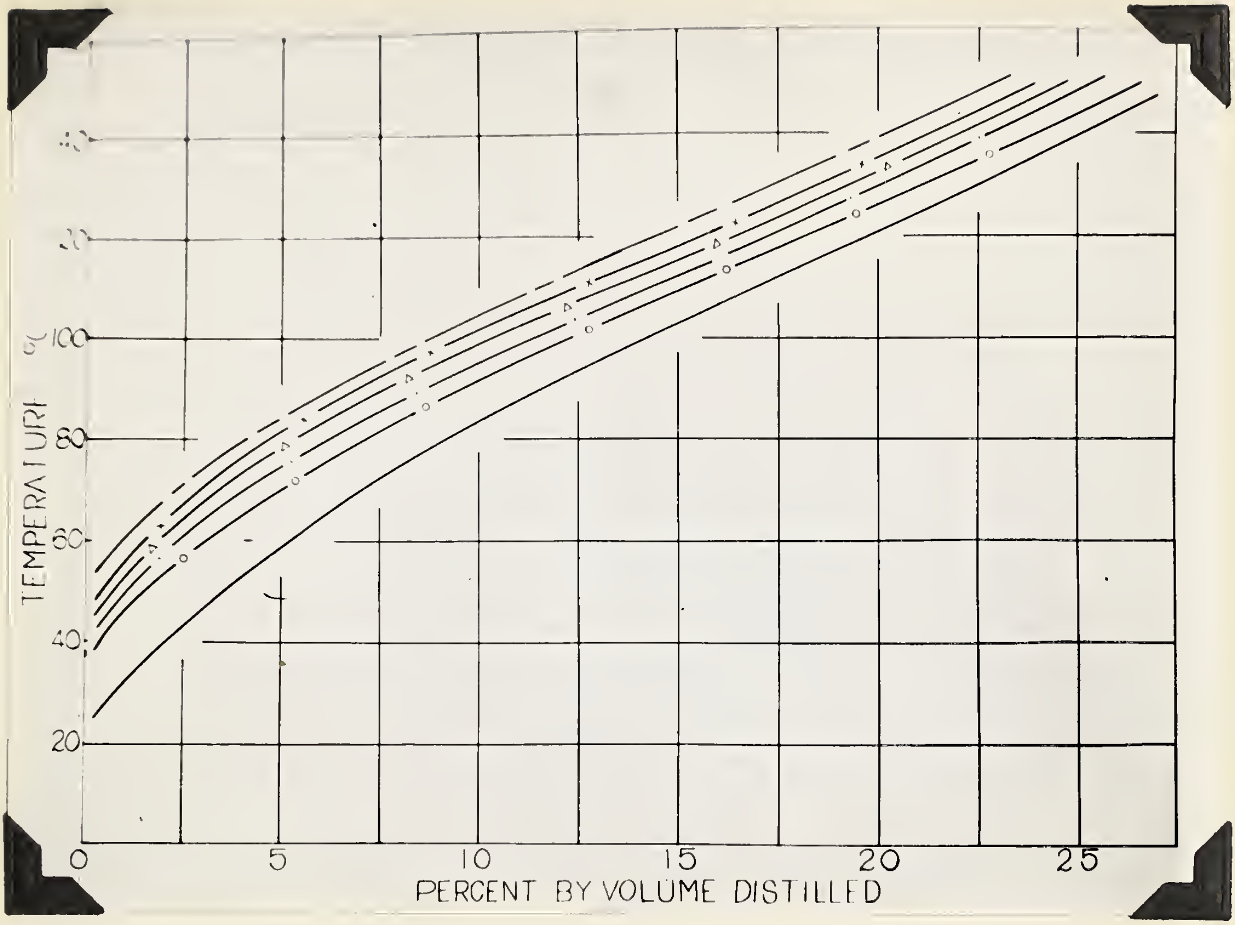


Figure II-2

Distillation Curves for Oil from Liquid Phase.

Gas/oil ratio 3:1

Original	———
500 p.s.i.	— o —
1000 p.s.i.	— · —
1500 p.s.i.	— △ —
2000 p.s.i.	— x —
2500 p.s.i.	— — —

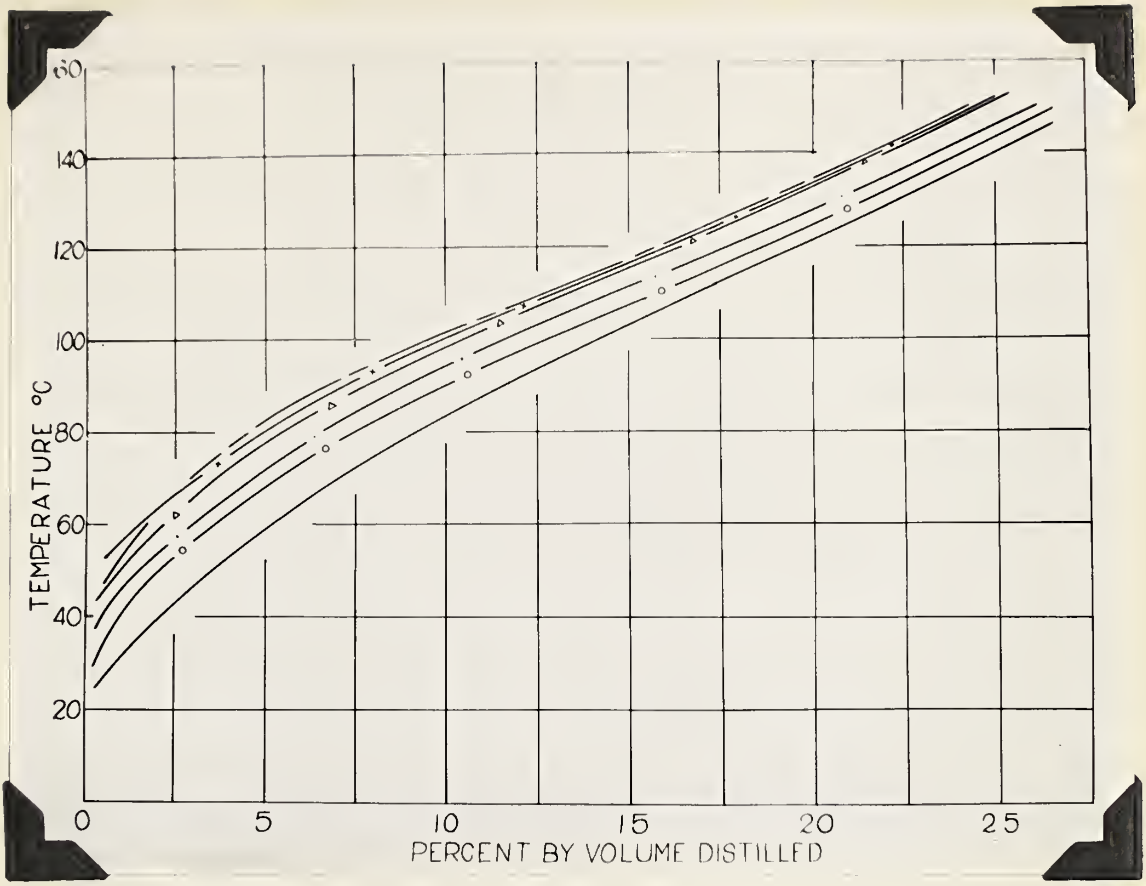


Figure II-3

Distillation Curves for Oil from Liquid Phase.

Gas/oil ratio 1:1

Original ————
500 p.s.i. —— o ——
1000 p.s.i. —— · ——
1500 p.s.i. —— △ ——
2000 p.s.i. —— x ——
2500 p.s.i. —— – ——

found to be true in the present case by inspection of the gas/oil ratios and Figure II-1. Due to the method by which the gas was liberated (2) only qualitative conclusions may be drawn from the vapor content of this gas. Due to the approximate establishment of equilibrium between the gas and oil at atmospheric pressure the vapor content is much higher than that found in the gas phase. This vapor content upon condensation corresponds to casing-head gasoline in the field. It will be related to the vapor or pentane content of the gas phase in equilibrium only in so far as the gas phase depletes the oil phase of lighter liquid hydrocarbons.

That the crude oil used in these experiments looses volatile materials to the gas phase is demonstrated by the distillations given in Table 3, and shown in Figure II-2 and II-3. The transfer of material from oil to gas in increasing amounts with increasing pressure is clearly shown and corresponds with the results discussed in connection with the gas phase composition. The amount transferred is relatively greater at lower pressures and on upper limit appears to be approached as the pressure is increased. The effect of differing relative volumes of gas and liquid phase is seen on comparing Figures II-2 and II-3, As expected, there is a greater transfer of material from the oil to the gas, the greater the gas volume relative to the oil volume. That the gas phases show much the same composition in both cases, merely means that in the proportions used here, there is much more than enough volatile material in the oil to saturate the gas.

SUMMARY

Apparatus and methods required to bring a Turner Valley crude oil and Viking natural gas into equilibrium in two phases at various pressures was described.

Assuming that conditions in the producing horizon of Turner Valley are an oil phase in contact with a gas phase, and neglecting the influence of the producing sand, conditions existing in the field have been reproduced approximately in the laboratory.

The solubility of natural gas in crude oil increases approximately proportionally with increasing pressure.

The density of the liquid phase decreases and its volume increases with increasing pressure. The density of the oil recovered after the removal of the dissolved gas is greater than that of the original crude oil. Distillation of the oil recovered showed that it contained an increasingly smaller proportion of volatile material as the pressure was increased.

The density of the gas phase increased with pressure and is always greater than the density of Viking natural gas at the same pressure. Amounts of pentane and higher hydrocarbons are found in the gas phase that vary with pressure, increasing rapidly at the higher pressures.

Transfer of the volatile constituents of the crude oil to the vapor phase in amounts depending, upon the pressure, has been demonstrated.

The results have been applied to the Turner Valley field in a qualitative way. The correspondence between laboratory and field data suggests that the naphtha wells in the Valley are fed by a gas cap above the crude oil area, or by a gas phase in connection with the crude oil area.

For more precise data, a number of refinements to the method employed must be made. Amore accurate means of determining the quantity of pentanes and higher hydrocarbons in the gas phase, and also an accurate method of duplicating the pressure in duplicate runs, are necessary to obtain quantitative results.

Part III.

PHASE EQUILIBRIA IN POLY-COMPONENT GAS-LIQUID HYDROCARBON SYSTEMS

The Pressure-Volume-Temperature relations in natural gases over the temperature range 25°C to 98°C, and the pressure range 0 to 200 atmos.

and

Apparatus, methods and preliminary experiments in the study of the behavior of the gas-liquid system composed of the whole product of a Turner Valley oil well.

INTRODUCTION

The physical equilibrium between coexisting liquid and gaseous phases has been the subject of much study for a number of years. Many simple systems of two components, and a smaller but growing number of complex systems have been investigated. The results of these experiments have been of theoretical and practical interest. The methods of thermodynamics have been of considerable assistance in prediction, correlation, and interpretation of the results. The work to be described in what follows deals with the properties and behavior of gaseous hydrocarbon mixtures, and two phase, gas-liquid hydrocarbon systems of natural origin. The work is a continuation of a general project dealing with similar systems of both synthetic and natural origin.

The determination of the P-V-T relationships of the gaseous state is a necessary preliminary procedure to study of the two phase gas-liquid systems. In addition, such information on the gaseous state is of theoretical and practical interest on its own account. The P-V-T relations of gases, whether expressed as empirical or theoretical equations of state, or in tabular or graphical form, throw light on the kinetic-molecular theory of matter and molecular forces, as well as provide data necessary to engineering calculations. Due to limitations of mathematical analysis and precise knowledge of molecular behavior, exact equations of state exist only in differential form.

Recourse is made to measurement, either to determine the coefficients of these equations as analytical expressions, or to devise empirical rules leading to expressions for P-V-T relations, requiring a minimum of experiment.

Only in the last decade have there been any extensive investigations into the phase relationships of liquid-gas hydrocarbon systems over wide ranges of temperature and pressure. These studies have been stimulated by theoretical interest in the theory of solution, and by the need for precise data on such systems, over a wide range of temperature and pressure, in petroleum engineering. Under what might be called ordinary conditions of temperature and pressure far below critical conditions, ideal or limiting laws, such as that of Henry, are generally satisfactory. However, it has been long recognized that the ideal laws are of value as expressing qualitatively a theory, and in application are subject to error, an error increasingly great as the temperature and pressure increase. In modern technology, the use of high temperatures and pressures is becoming increasingly common, leading to a demand for more precise expression of the behavior of matter.

The purpose of the current work in this laboratory is twofold. It is hoped that the results will be useful in interpretation of the history of the Turner Valley oilfield, and in providing data for proper operation with a view to optimum production. Second, the results do provide a means of examining and expanding the theoretical aspects of the subject.

The work was started in 1931 with studies of simple two component systems. These investigations could have been extended without limit, but, when a method had been established, it was thought advisable to investigate complex polycomponent systems more nearly related to practise. Gillies and Hugill (8) investigated a complex system from a Turner Valley gas cap well, which may be described as limestone zone natural gas and naphtha. Davis and Boyer (1940) made preliminary studies using a Turner Valley limestone zone crude oil and Viking natural gas.

The present work was carried out using the gas and crude oil from a well penetrating the Palaeozoic limestone in the Turner Valley Field. A new apparatus was devised for studying this equilibrium. Pressures, temperatures, and gas-oil ratios may be varied at will within wide limits. Samples of the liquid and gaseous phases in equilibrium may be taken for analysis.

In addition, the P-V-T relationships of the natural gas was determined as information necessary to the main work described above. The fugacity, and thermodynamic properties of the gas at various pressures has been determined. Lewis' fugacity rule (18) has been tested using the data obtained here, and also by other workers on other natural gases.

Time did not permit a complete series of equilibrium measurements to be made on the two phase system. However, sufficient data were obtained to prove the method, and to indicate the character of the results which may be obtained with the new

apparatus.

In appendix I, is described a new portable gas analysis apparatus, embodying all the essential parts for the analysis of hydrocarbon gases.

LITERATURE

During the past few years, a large bibiography on the equilibrium in hydrocarbon systems has been accumulated. Johnson (12) and Piercey (23) have given a very comprehensive review of the literature on solubility in simple systems. Gillies and Hugill (8) have covered the literature concerning more complex hydrocarbon systems. In this report, it is proposed to refer to only those papers which have been published during the past year, or which have a direct bearing on the present work.

Since the larger proportion of results in this project concern P-V-T relationships in the gaseous state, the literature on this subject will be considered first. The behavior of methane, and the computation of its thermodynamic properties has been given by Sage and Lacey (29), and by Kvalnes and Gaddy (16). The data for ethane used in the present work is that due to Sage and Lacey (29), and for propane is due to Sage, Schaafsma and Lacey (31), and to Deschner and Brown (4). Sage et. al. have also provided data on butane (32), and on pentane (30). The data, given in these papers, have been chosen as the most reliable, and are used in this thesis in correlating the behavior of the natural gas used with composition. In the application of Lewis' fugacity rule to the natural gases, the fugacities of the components were computed from the data given in these references.

Robinson and Bliss (25) have derived equations for calculating entropy, enthalpy, and energy changes in terms of volume from the equations of state of Van der Waal's, Wohl, and Beattie-Bridgeman. These have been tested against published values determined graphically. The Beattie-Bridgeman equation is satisfactory to five to seven per cent for entropy, and twelve per cent for enthalpy determinations. The others are almost as good for entropy calculations but definitely inferior for enthalpy.

Computation of the fugacity of the gases from P-V-T data followed the method of Lewis and Randall (18), based on "residual volumes" and graphical methods of integration. Thermodynamic properties were computed by means of well known differential equations using both analytical and graphical procedures. The methods, to be described more fully later, are well illustrated in general form by Edminster (6), and applied particularly to methane.

While many papers have been published on simple two component hydrocarbon systems, few have been published on the system natural gas-crude oil. Miller (20) has pointed out the function of natural gas in the production of crude oil. It is necessary to have a complete picture of the phase relationships before an understanding of crude oil production is obtained. Lacey (17) showed that a hypothetical producing horizon, producing natural gas and liquid hydrocarbons with a normal boiling point of 200°C and higher, could, at a sufficiently high pressure

contain only a single saturated gas phase. The fact, that increased pressure should vaporize and decreased pressure condense, is in contradistinction to normal behavior at near atmospheric pressure. The phenomenon is not new (12), and is exhibited by two phase, two component or polycomponent systems of either type gas-liquid or gas-solid. This phenomenon, known as retrograde condensation, plays an important part in crude oil production. This has been clearly expressed by many workers, and particularly by Katz and Kurata (14).

Sage and Lacey (27) reported investigations on natural gas and crude oil from the California Dominguez field. Katz and Hachmuth (13) studied the equilibrium constants in a system of natural gas and crude oil, over a pressure range of one to two hundred atmosphers, and a temperature range of 40° to 200°F. They show that the equilibrium constants for methane ethane, propane, butane, pentane, hexane and heptanes plus, converge towards one at the critical pressure of complete mutual solubility of both phases.

Sage and Lacey (28) have attempted to correlate the equilibrium constant for methane in a variety of hydrocarbon systems, on the basis of the prevailing pressure, temperature, molecular weight, and chemical nature of the components other than methane in the system. Their results are applicable in predicting the behavior of methane in producing horizons. In this connection, Nederbragt (21) has pointed out that the equilibrium constants for methane should become higher if naphthenes and other aroma-

tics are present. Methane is less soluble in these than in members of the paraffin series.

From his work on the systems ethane-normal butane, and ethane - normal heptane, Kay (15) concludes that qualitatively, the higher the molecular weight, i.e. the higher the critical temperature of the solvent, the greater the temperature and pressure range over which the mixtures approximate perfect solutions. This has been shown clearly by Johnson (12), and in addition, that the critical pressure increases regularly with molecular weight and boiling point of the liquid component.

Gilliland and Scheeline (9), from their work on two component hydrocarbon systems, conclude that the equilibrium constants for hydrocarbons are in considerable error around the critical region of the system. They suggest an empirical correlation for predicting phase equilibrium data in the critical region for two component hydrocarbon systems. For pressures below the critical, the experimental values are satisfactory.

As pointed out by Ewell (7), verification of Lewis' fugacity rule would be very useful in calculating equilibrium constants used in considering chemical reactions at high temperatures and pressures. No thorough test of Lewis' fugacity rule has been made however.

THEORETICAL

The study of the gaseous and liquid phases in physical equilibrium have given rise to many expressions relating the composition of the phases. Probably the simplest quantitative relations applied to two component systems are Henry's Law and Raoult's Law. These are applicable only to ideal solutions and assume that the properties of the liquid are unchanged by pressure. They may only be applied to hydrocarbon systems at low pressures.

Poynting (24) showed that the pressure on a liquid influenced its vapor pressure according to the relation -

$$\left(\frac{dP_1}{dP_2}\right)_{T.X.} = \left(\frac{\bar{V}_2}{\bar{V}_1}\right)_{T.X.}$$

where P_1 = vapor pressure of liquid

P_2 = total pressure on liquid

$\bar{V}_2$ = partial molal volume of liquid

$\bar{V}_1$ = partial molal volume of vapor

The equation is exact but describes only point conditions. In its application to the prediction of the behavior of the two phase system, integration is required. Various integrations have been carried out under different assumptions, the principal one being that the gas used to create pressure on the liquid is not soluble in the liquid. Obviously, this is not even approximately true for the systems dealt with here. In the present case, integration requires a knowledge of $\bar{V}_1$ and $\bar{V}_2$

as functions of the pressure on the system and the composition of both phases. In other words, an extensive series of measurements on the system is necessary.

A differential equation may be derived for each of the two phases in equilibrium. However, the practical application of these equations depends on the experimental evaluation of the coefficients. Boomer and Johnson (1) have pointed out that this presents considerable difficulty.

P-V-T Relationships

As has been pointed out previously, exact mathematical expressions for the P-V-T behavior of the gaseous state exist only in the differential form. A number of empirical equations of state for gases have been proposed, but each is suitable only within the limits for which it was devised. While empirical equations of state are used to a large extent in engineering calculations, the fugacity, as proposed by Lewis and Randall (18) has probably a wider application. In the present work, the fugacity was determined by evaluating the relation -

$$RT \ln \frac{f}{P} = -\int_0^P a\,dP$$

where f = fugacity
a = "residual volume"
$= \frac{RT}{P} - V$
P = pressure
V = volume
T = degrees Kelvin
R = gas constant

The residual volume, a, is thus the difference between the actual volume and the ideal volume of a gas. The value of the

integral $\int_0^p a\,dP$ was obtained by graphical integration.

In considering the pressure of a gas mixture, Dalton's law applies only to mixtures that may be considered as ideal, i.e. at low pressures. This law is of little value in the present work and recourse must be had to fugacity. Lewis (18) has proposed the following rule for the fugacity of a gaseous mixture -

$$f_1 = N_1 f_1^\circ$$

$$f_t = f_1 N_1 + f_2 N_2 + \text{---------}$$

where f_1 = fugacity of a component in a gaseous mixture.
N_1 = mol fraction of the component in the mixture
f_1° = fugacity of the pure component at the same temperature and total pressure as the mixture.
f_t = fugacity of the mixture

Verification of this rule would enable the fugacity of the gas to be calculated from an analysis, given the fugacity-pressure relations for the pure components. These latter relations are known for many gases, and in particular for the paraffin gases.

Solubility Measurements

The Gibb's Phase Rule indicates that the simple two component, gas-liquid system is univariant. This system may be represented graphically on this basis. The representation of a polycomponent system, such as the present one, is more difficult. As has been pointed out above differential equations may be derived for each phase, but the evaluation of the co-

efficients, from experiment is exceedingly difficult.

Probably, the so-called equilibrium constants serve best to describe the systems. Furthermore, empirical rules describing the variations in these constants should be simple. The equilibrium constant may be defined in the ideal case as -

$$K = \frac{C_1{}^G}{C_1{}^L}$$

where $C_1{}^G$ = concentration of the component in the gas phase.
$C_1{}^L$ = concentration of the component in the liquid phase.

True constants can be expected only if both the liquid and gaseous phases behave ideally; which they do not do. Hence the true constants, determining the free energy of the components, can be found only from a knowledge of the activities of the components. Expressions relating equilibrium constants to the properties of the components of the system, pressure and temperature, can be established only when the fugacities or activities of the components in each phase are known.

While in the present report insufficient data have been collected for the establishment of empirical relations, the results of the experiments will be discussed qualitatively.

EXPERIMENTAL

A preliminary series of experiments were carried out using samples of natural gas and crude oil from the Home-Millarville #3 well in Turner Valley. The gas mixing and storage system proved unsatisfactory, and was redesigned for the present work. A second set of samples were obtained from Alberta Oil Incomes #2 well.

In January, 1941, when the samples were taken, this well produced 45 barrels of crude oil daily, at a gas/oil ratio of 600 cu. ft. per barrel. The bottom hole pressure was 2750 p.s.i. and the bottom hole temperature 198^{o}F. This well was the farthest north producing well in the Turner Valley field, being located in the centre of LSD. 4, Section 4, Township 21, Range 3, West 5th M.

The gas sample was taken through a $\frac{1}{2}$ inch valve on a 3 inch fuel line from the separator. The oil sample was taken through the bottom valve on the oil level gage on the separator. Eight standard gas cylinders were used to collect the gas sample, while the liquid sample was taken in a liquid bomb. The bomb was first filled with water and as the oil was collected, the water was drawn from the bottom. About 1/8 of the water was displaced from the bomb, while one cylinder was filled with gas to a pressure of approximately 200 p.s.i. Samples were taken slowly over half hour intervals of time. A total time of four hours was required in filling the eight cylinders. During this

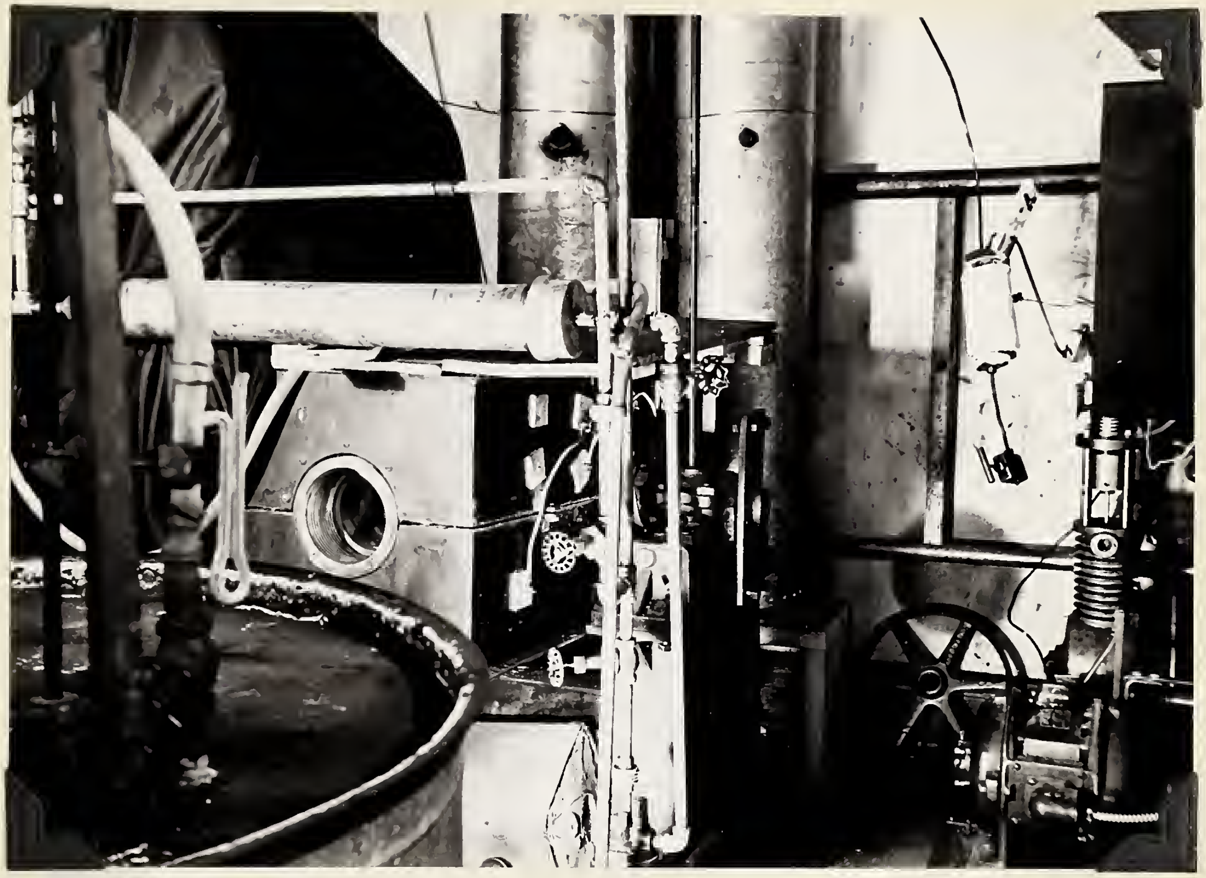


FIGURE 1 - The Gas Storage System and Compressor.

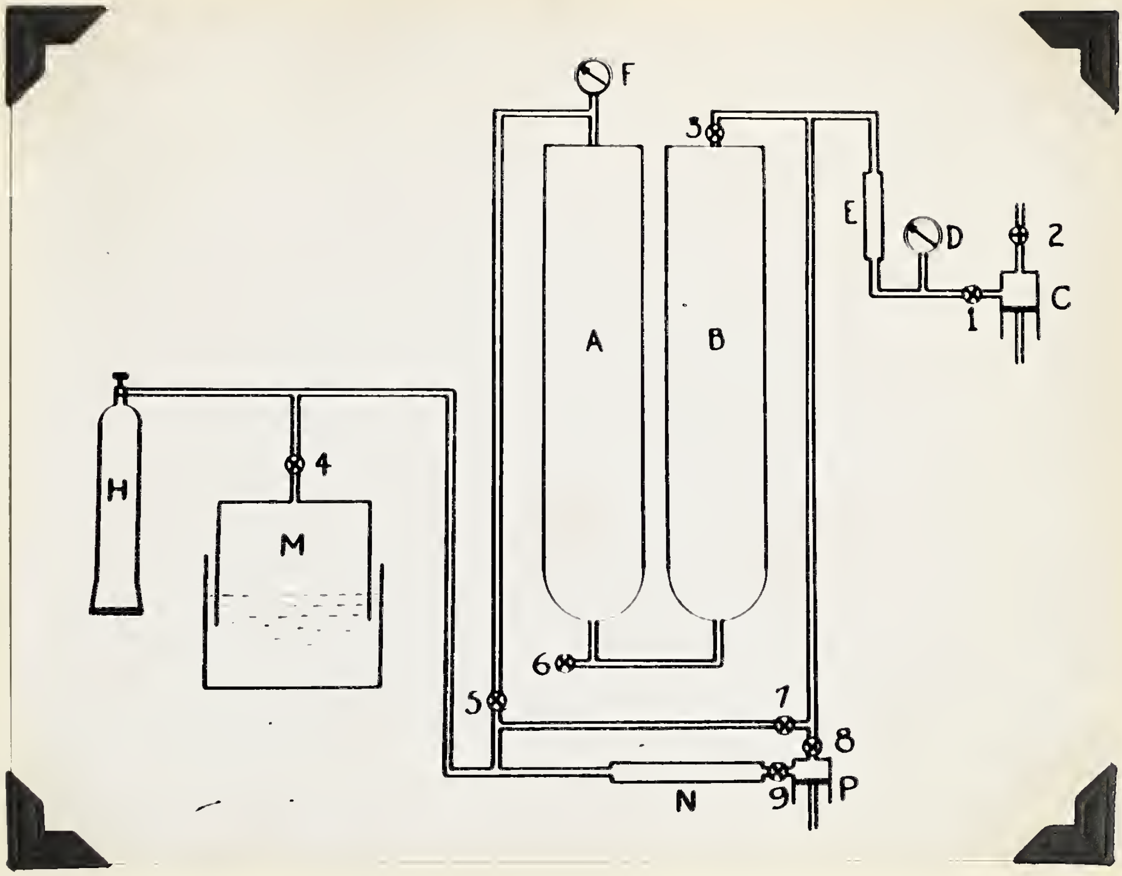


FIGURE 2 - Diagram of the Gas Storage System.

time, the well operated steadily at 19 bbl./hr. and a gas/oil ratio of 700 cu.ft./bbl. Sampling was carried out by the field staff of the Petroleum and Natural Gas Conservation Board, supervised by Mr. G.A. Connell.

The samples were treated in the laboratory as follows -

The gas sample was bubbled through 20% potassium hydroxide solution in a glass tower, packed with short lengths of glass tubing, to remove hydrogen sulfide and mercaptans (23). The scrubbed gas was stored in the gas holder M (Figure 2). From the gasholder, the gas was pumped into the low pressure storage tanks A and B by compressor P. It was dried over calcium chloride in N. Each cylinder of gas was transferred in this manner to low pressure storage. Because of minor variations in composition in different cylinders, it was necessary to mix the whole gas throughly. Three gasholders in parallel were used in mixing operations. Gas from A and B was expanded to the gasholders through valve 5, and compressed again by compressor P. Gage F indicated the pressure of the gas in the storage tanks. The gas was circulated until a constant analysis was obtained.

The liquid sample was displaced from the bomb by water, and scrubbed with 20% potassium hydroxide solution in the glass-packed tower. The gas, liberated from solution in the oil, was collected in a gasholder, and pumped into the low pressure storage tanks A and B with the gas sample before mixing. The

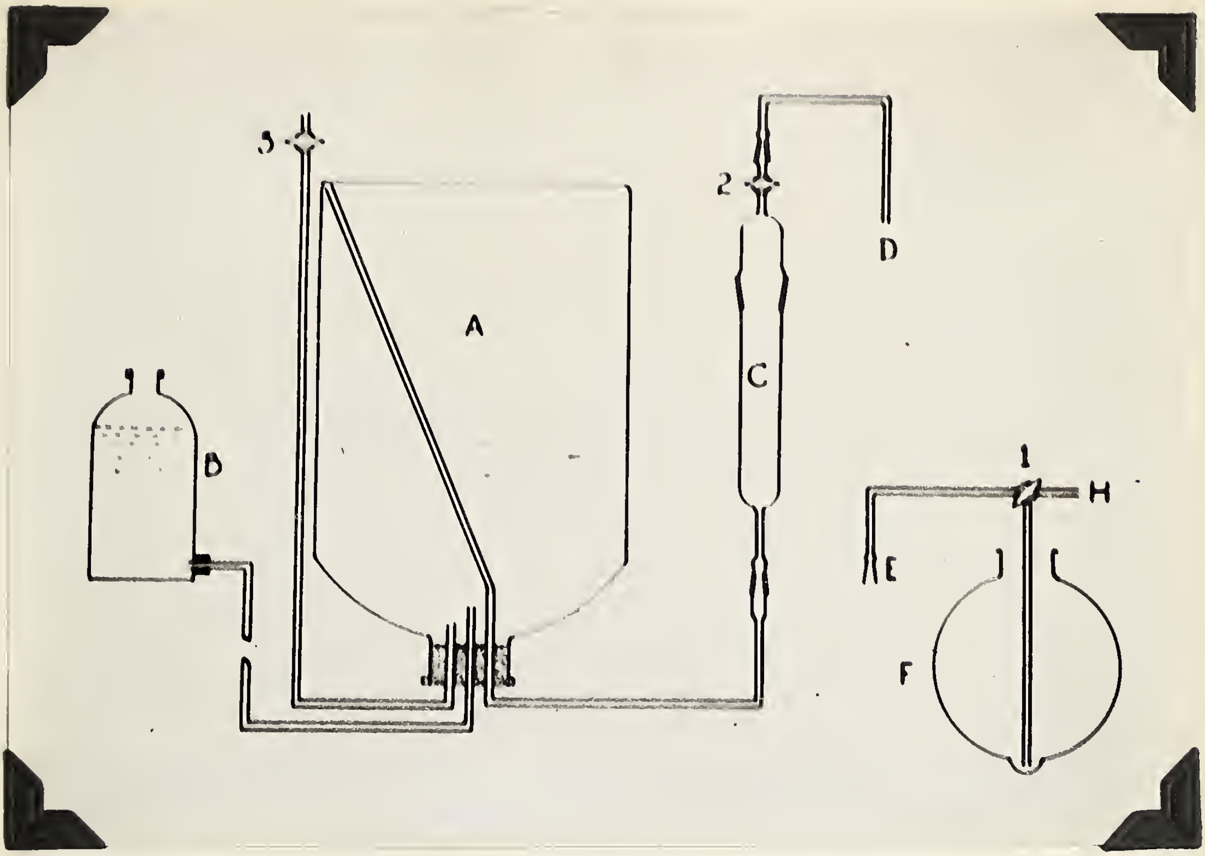


FIGURE 3 - Diagram of the Crude Oil Storage and Dispensing System.

oil line was connected at stopcock 3 (Figure 3) and the oil collected over water in carboy A.

The composition of the gas was determined by analysis with the low temperature fractional distillation apparatus (8) (See Appendix I). The average of nine analyses gave -

Component	Vol.%
methane	78.40
ethane	12.49
propane	4.59
butane	1.56
pentanes +	0.54
nitrogen	2.42

The density of the gas was determined in the conventional manner, - by weighing a calibrated bulb, containing the gas at a measured temperature and pressure. The average of a large number of determinations gave the following result -

$$d^{25^\circ C}_{76cm} = 8.278 \times 10^{-4} \text{ gm/ccm.}$$

The average deviation from this mean, was five parts in a thousand. The reason for this large deviation could not be determined with certainty, but is probably connected with the pentane content of the gas. That the method was satisfactory, was shown by duplication of results to 0.1%, using dry air.

The density of the crude oil was determined gravimetrically at two temperatures -

$$d^{20^\circ}_{4^\circ} - 0.8119 \text{ gm/ccm}$$

$$d^{25^\circ}_{4^\circ} - 0.8075 \text{ gm/ccm}$$

A precise fractional distillation of the crude oil in a Davis type column gave the following results for the more volatile portion:

Temperature °C	Vol.% Over
30	2.0
40	2.2
50	2.7
60	3.6
70	6.0
80	12.0
Residue	88.0%

These results are the average of five distillations and show 2 to 2.2% pentanes and lighter in the oil.

A fractional distillation of the crude oil in an 18 inch glass column, vacuum jacketed and with controlled reflux, gave the following results:

Overhead Temperature °C	Vol % Over
25	Initial Boiling Point
25	1
25	2
28	3
32	4
48	5
58	6
72	8
85	10
106	15
124	20
144	25

The mean molecular weight of the crude oil was determined by the cryoscopic method (8), and was 179.4 ± 1%.

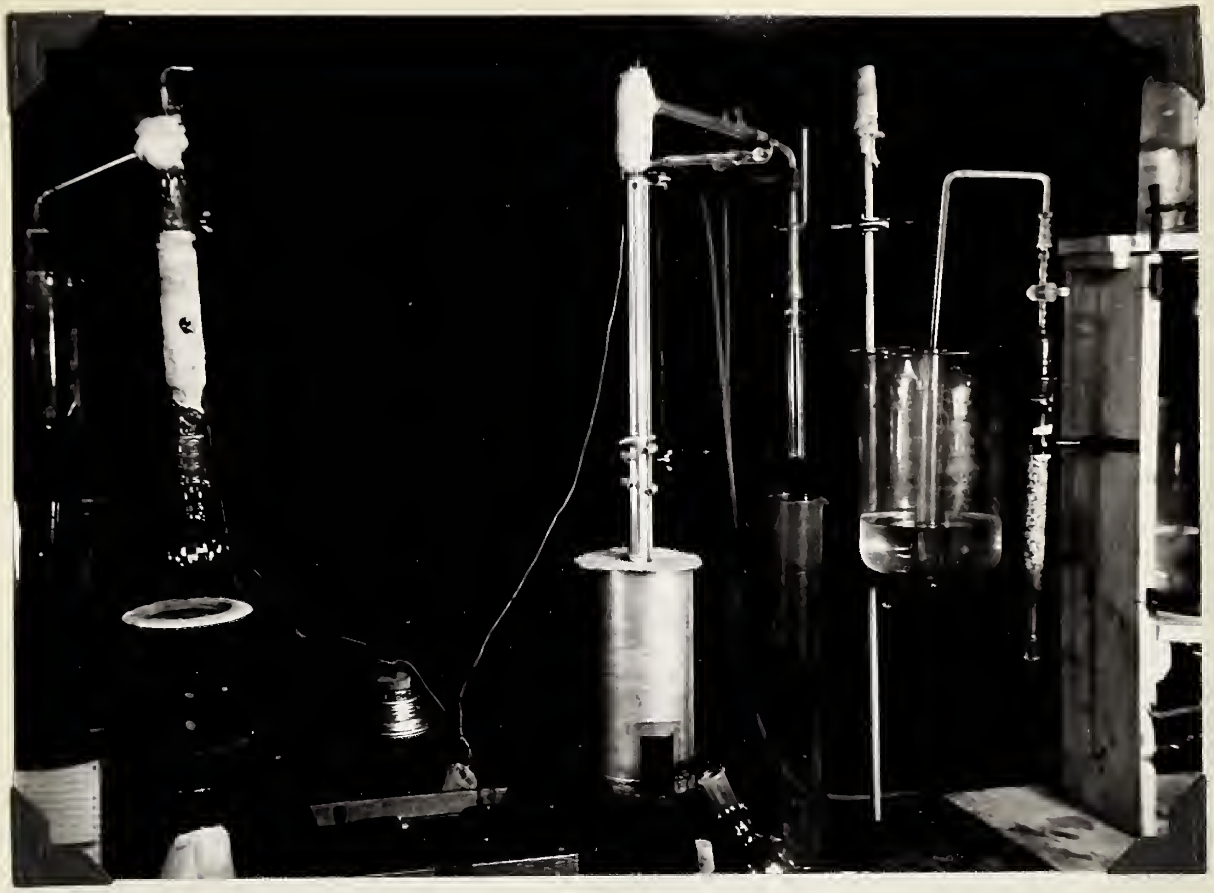


FIGURE 4 - The Fractionating Columns, and the Crude Oil Dispensing System.

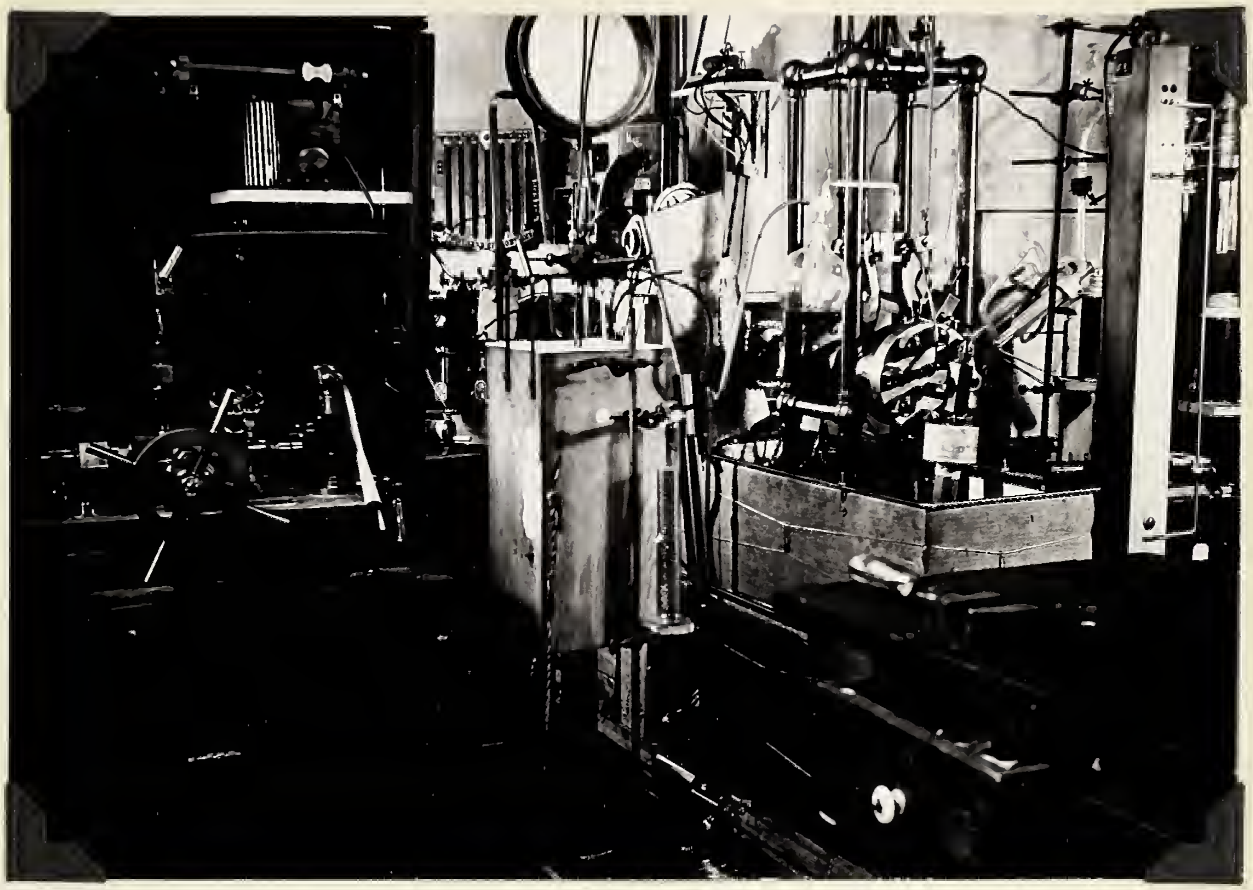


FIGURE 5 - The High Pressure Apparatus.

Apparatus

The experimental apparatus may be described conveniently under three headings -

1. High pressure system and equilibrium cylinder.
2. Low pressure analytical system.
3. Crude oil storage and dispensing system.

The high pressure system is shown diagrammatically in Figure 6. It consists essentially of drier K, high pressure gas measuring pipette M, deadweight piston gage A, and equilibrium cylinder P. The natural gas from storage (Figure 2) is admitted to the system through the booster compressor D (Figure6). It enters the drier K through valve 4, and is admitted to the pipette M through valve 5. The system may be opened to the atmosphere E, through valve 3. The drier K is filled with potassium hydroxide pellets and is surrounded by an air bath H. The temperature of the air bath is kept near 60°C, by means of a 450 watt heater. The Bourdon gage F indicates approximately the pressure in the drier or the pipette. The measuring pipette is surrounded by a thermostatically controlled oil bath, whose temperature is maintained at 60°C ± 0.15°. Valve 6 connects the pipette to the piston gage and the equilibrium cylinder. The pipette is connected through valve 8 to a hydraulic pump N, fed by mercury. Mercury may be drained from the pipette through blow off valve 7.

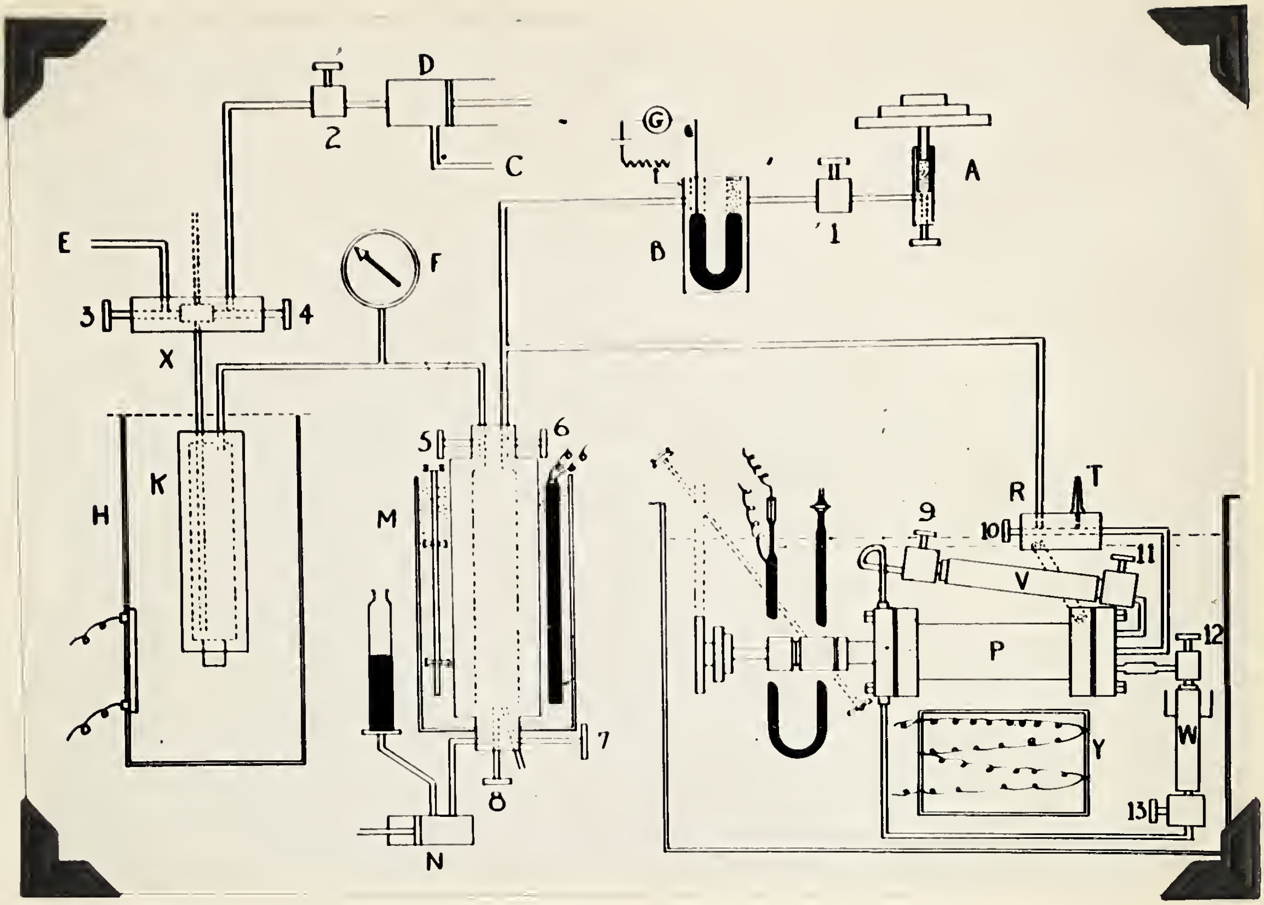


FIGURE 6 - Diagram of the High Pressure System.

Valve 1 connects the deadweight gage A to the system. A mercury U-tube B, is placed in the line. The gas leg of the U-tube is equipped with a blow off valve. An insulated lead terminates in a platinum point at the surface of the mercury. A galvanometer, dry cell, rheostat, and a lead grounded to the U-tube complete the circuit. The deflections on the galvanometer when the mercury contact is made or broken, indicate the level of the mercury. The U-tube is necessary to prevent solution of the gas in the castor oil of the piston gage.

The equilibrium cylinder P is immersed in a thermostatically controlled oil bath. The bath is heated by two 1500 watt heaters Y, one of which is connected to the relay circuit. The cylinder is supported in the bath, on two metal cradles. It is raised from the bath by a screw jack and cable device.

Gas from the measuring pipette is admitted to the cylinder at R through the charging valve 10. T is a standard taper, steel, male connection, to which may be attached the liquid and gas measuring device, operated at atmospheric pressure and to be described later. The bore of the connection is threaded and has an internal seal, to fit a hardened steel closure plug. To the cylinder are connected a gas sample pipette V and a liquid sample pipette W.

To eliminate the possibility of condensation of pentanes and butanes in the gases used, under the influence of the high pressures employed, provision is made to maintain all high pressure gas lines and containers, including the booster com-

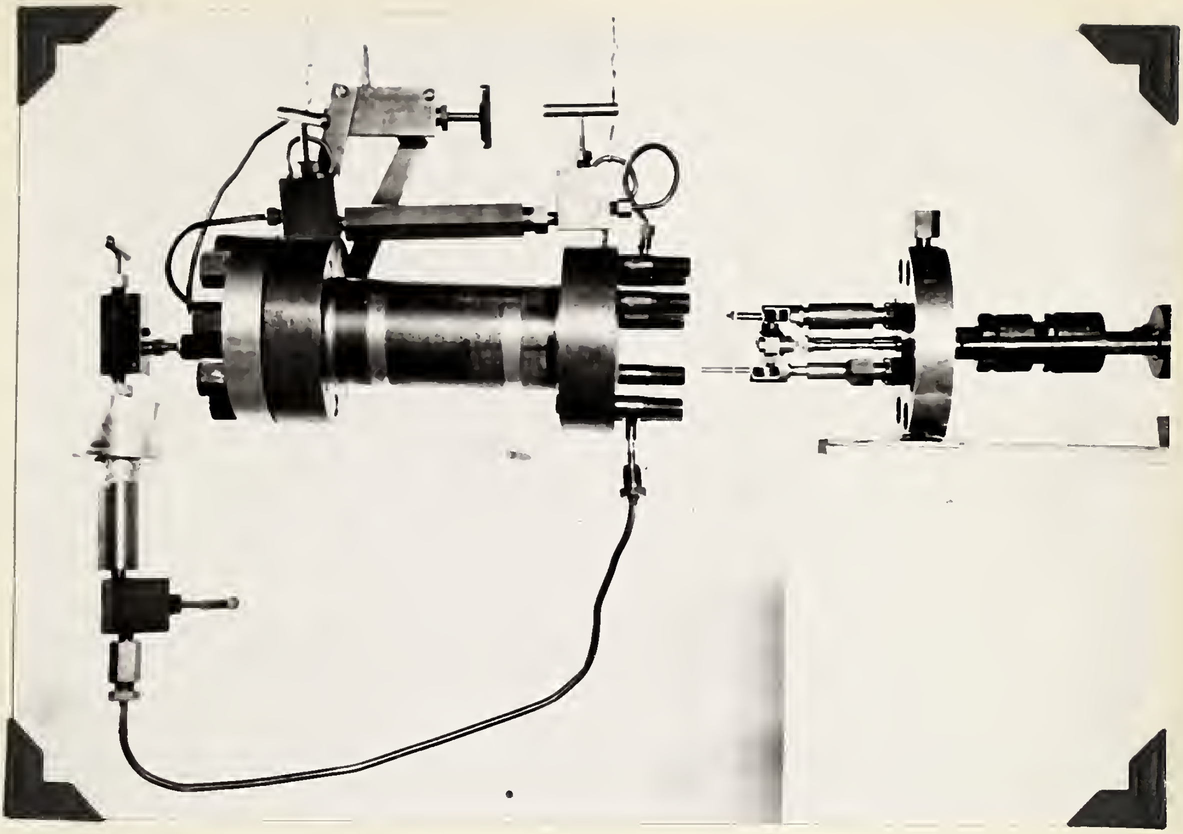


FIGURE 7 - The Equilibrium Cylinder Assembly.

pressor, at about 60°C. The gas lines of 1/16" x 1/4" steel tubing, are heated by a low voltage, high amperage current, obtained by means of a transformer fed by the laboratory supply at 110 volts. The booster compressor and oil trap are heated by wire type metallic resistors on 110 volts. The steel U-tube separating the gas from the piston gage is heated by a low voltage wire type resistor. The methods of heating the high pressure drier and measuring pipette have been described.

The equilibrium cylinder constructed of stainless steel, is 4" O.D., 3 1/16" I.D. and 12½" long. On each end is threaded a 2" steel collar 7" in diameter (Figure 8). The ends of the cylinder are constructed of stainless steel plates, 1 3/8" thick and 7" in diameter. These plates are attached to the cylinder by 8, 1" heat-treated steel bolts, 4½" long, placed symmetrically around the steel collar (Figure 7). Copper gaskets between the cylinder and end plates make the closure gas tight.

The inner end of a bearing and packing gland carrier is screwed into the centre of one of the end plates, a tight steel to steel joint being formed by a suitable seat in the end plate. The construction of this carrier and the drive shaft passing through it, is clearly shown in the scale diagram (Figure 8). The dotted lines represent alternate layers of plastic metallic packing and graphited asbestos packing. The packing is compressed by a gland follower on adjustment of the packing nut as shown. Two steel pedestals mounted on the end plate carry a

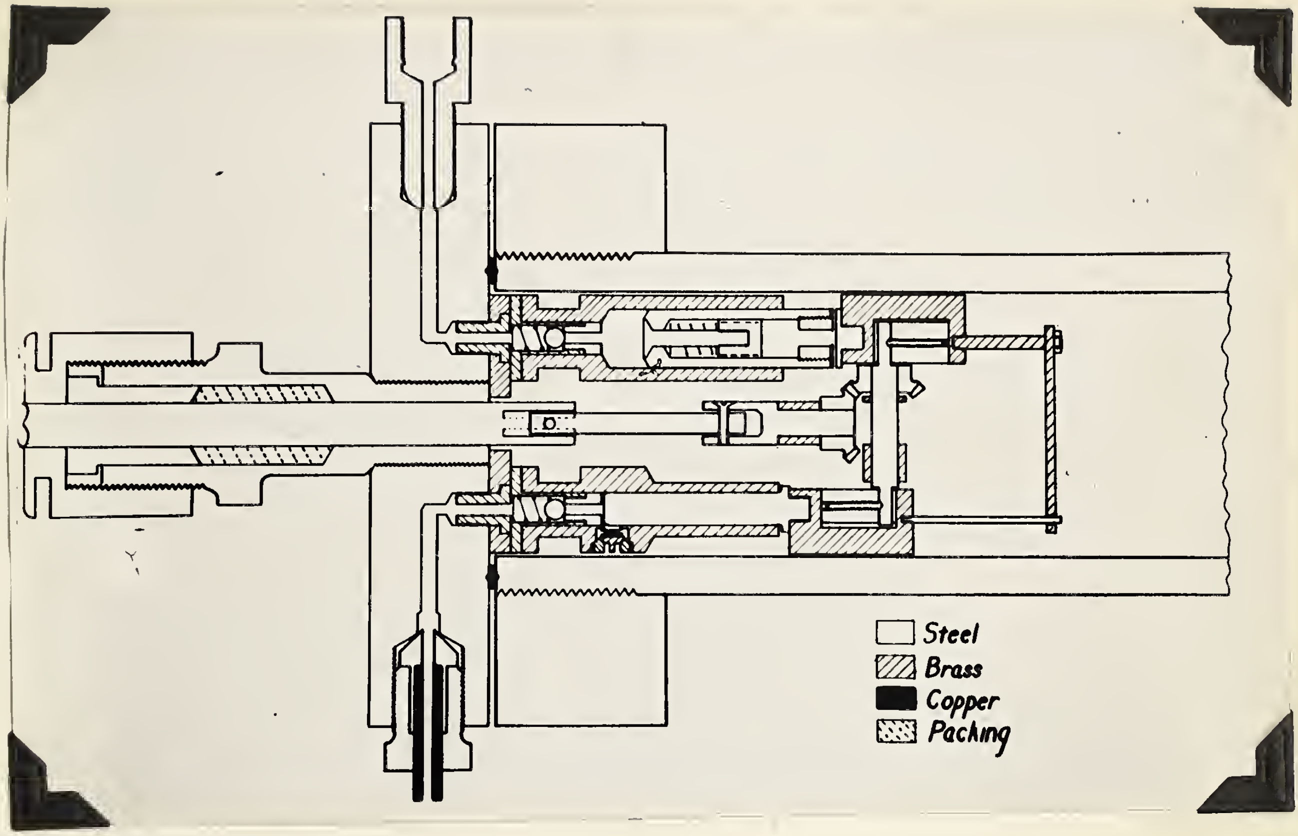


FIGURE 8 - Diagram of the Pump assembly.

casting fitted with a ball thrust bearing, through which the drive shaft passes. On the outer end of the drive shaft is fitted a sprocket wheel to take the driving chain.

Two 3/8" holes, ½" deep are drilled and threaded on a vertical diameter, 1" above and 1" below the centre of the end plate from its inside face (Figure 8). From the bottom of these two holes are drilled two 1/8" holes to meet two 3/16" holes drilled from the circumferential face of the end plate. At the top circumference face, the 3/16" hole becomes 9/16" in diameter, threaded and seated to fit an adapter, permitting connection with 1/16" x 1/4" steel tubing by a standard joint, used in this laboratory. The 3/16" hole to the bottom circumference face is expanded first into a 1/4" hole 1/4" deep which in turn becomes a 3/4" hole threaded and seated to fit the connector on 1/8" x 5/16" copper tubing.

This connector consists of a steel collar threaded and sweated on to the copper tube. The end of this collar is 11/16" in diameter. The face is machined at an angle of 45° to the axis of the collar (Figure 8). The body of this collar is 3/4" long and 13/32" in diameter. A follower, fitted with 3/4" threads, fitting over the body of the collar serves to seat the face of the collar as shown. A similar assembly is attached to the other end of the copper tubing.

All threaded parts are cut to standard S.A.E. specifications.

The pump assembly is attached to the inside face of the end plate by two steel plugs, 3/8" in diameter by 5/8" long

screwed into the end plate. These plugs have a 1/8" flange at their outer end, 9/16" in diameter, into which is cut a screwdriver slot. This flange holds the pump base plate to the end plate (Figure 8). A 1/8" hole to serve as a discharge conduit for the pumps is bored through the plugs. The pump base plate of 1/4" thick brass plate is 3" in diameter. A 5/8" hole at its centre permits the passage of the main drive shaft into the cylinder. Two steel pedestals are mounted on the base plate, on a horizontal diameter and 1" on each side of the centre. They carry an upper and a lower brass bearing, the lower one for the shaft of the driving mitre gear, and the upper one for the shaft of the driven mitre gear. On the vertical diameter of the base plate and 1" on each side of the centre, two 9/16" holes, 1/8" deep, which decrease to 3/8" holes for the remaining 1/8" of the plate are cut. These holes take the two steel plugs which hold the base plate to the end plate. The cylinder heads are situated over these two holes and each is connected to the base plate by six 1/8" brass bolts, 3/4" long. These bolts are countersunk in the underside of the base plate.

The cylinders are constructed in one piece from 1" hexagonal brass rod. Except for a 1/8" base flange, and in the case of the liquid pump over a 3/4" length carrying the intake valve, the cylinders are machined to a cylindrical cross-section.

The liquid cylinder of 5/8" outside diameter, except as noted above, and of 3/8" inside diameter is 3" long. A small cone shaped intake valve backed by a light spring fits a valve seat screwed into the bottom side of the cylinder opposite to the end of the piston stroke. This type of intake valve performs satisfactorily in the liquid pump but cannot be used in the gas pump. The exhaust valve, a 1/4" ball backed by a light spring is carried in a flanged tube 5/16" I.D. and 3/8" O.D. to fit the cylinder bore as shown. The piston for the liquid cylinder is a 3/8" steel rod, flanged at one end, terminating above the flange as a 1/4" threaded bolt.

The gas cylinder of 1" O.D. and 3 1/16" long is bored to take a 11/16" diameter piston for a distance that leaves 1/16" clearance at the end of the pumping stroke. From this point to the flanged bottom, the cylinder is bored to 3/8" diameter to fit an exhaust valve identical with that on the liquid cylinder. The piston itself carries the intake valve in its hollow interior, gas being admitted through six 1/16" holes, bored through the flange at the outer end of the piston. The valve, of steel, is of the conical type with stem, backed by a light spring and fits a seat cut in the piston head. The hexagonal flange at the outer end of the piston, cut from a 3/4" hexagonal bar, screws into the hollow piston and terminates at its outer end in a threaded 1/4" bolt.

Identical U-shaped brass guides are screwed to the piston

ends. These guides are cut to have a 15/16" clearance between the inside of the arms of the U and fit cylindrical steel driving cams, 7/8" in diameter. The construction of the driving mechanism is self explanatory from Figure 8. The brass sections represent the bearings and U-bars. The gears are 7/8" steel mitre gears. The driven gear carries a shaft terminating at each end in a driving cam. The centre line of the shaft is 1/4" removed from the centre of the cams, thus producing on rotation a ½" stroke in the pumps. The driving gear is connected to a short driving shaft by a flexible, pinned joint. The other end of this shaft is connected to the end of the main drive shaft by a similar joint. This makes in effect a simple universal joint necessary to absorb any small lateral displacement between the drive shaft and pumping mechanism.

The end plate closing the other end of the cylinder is of relatively simple construction. It is the same size as the other plate, and is attached to the cylinder in the same manner (Figure 7). It is fitted with three holes, 1/2" deep and threaded to 9/16" S.A.E. standard in order to take the standard tubing connectors used. Fluid passages, 1/8" in diameter, extend from the bottom of the holes through the end plate. Two holes are on the vertical centre line, and the third is to one side on the horizontal centre line. An adapter of 1" round chrome molybdenum steel bar with 9/16" S.A.E. threads on one end fits the lower hole in the end plate. The adapter, 4¼"

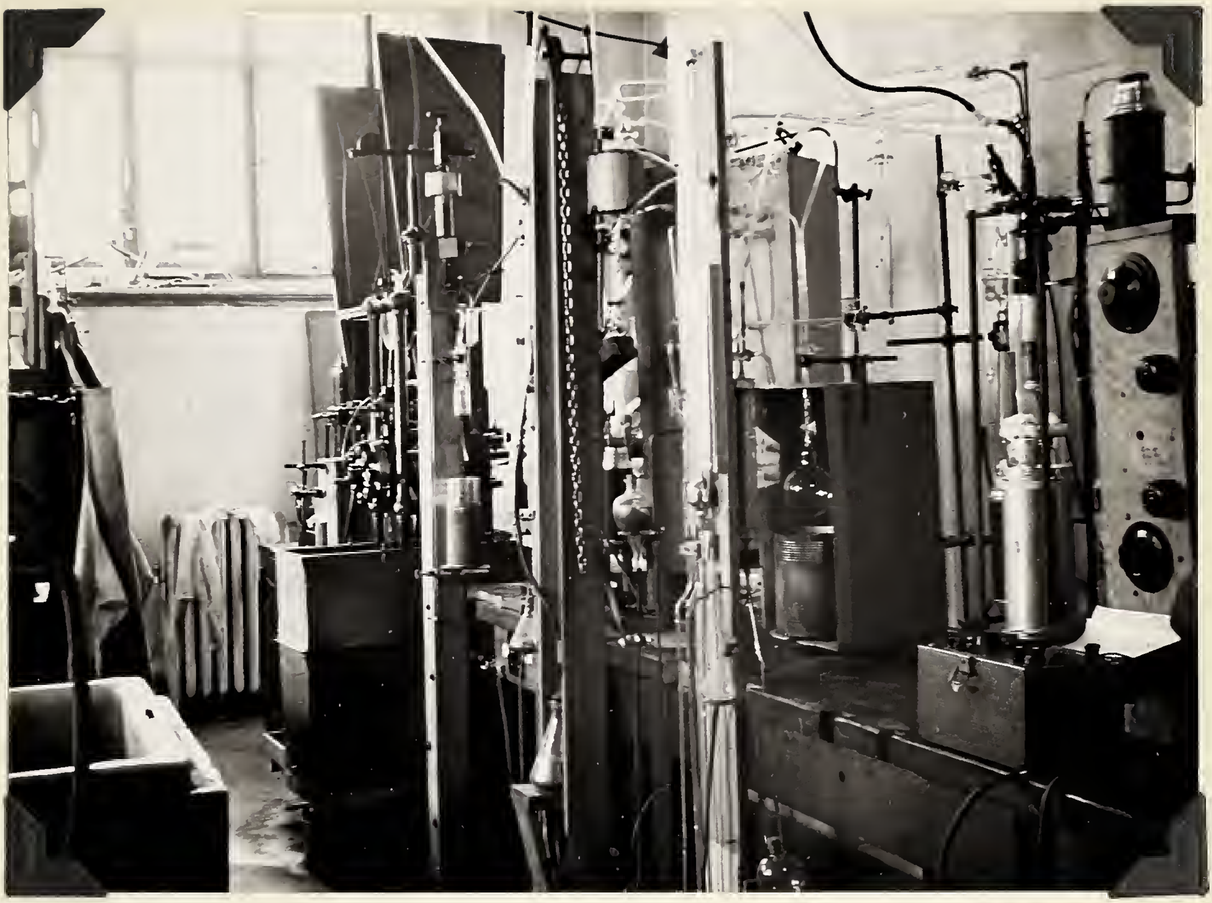


FIGURE 9 - The Experimental Apparatus.

long, is fitted at its other end with a standard connector for the valve of the liquid sample vessel (Figure 7).

The upper hole in the end plate is connected by 1/4" steel tubing to the valve on the gas sample vessel with standard connectors. The third hole in the end plate is connected by 1/16" x 1/4" steel tubing and standard connectors to the charging valve as shown.

The steel sample vessels or pipettes are connected as illustrated in Figure 7. The gas sample pipette which is situated along the top of the equilibrium cylinder is constructed from a 1¼" hexagonal steel rod 7" long. A ¾" hole tapered at the bottom and 5½" long is drilled in the rod. The open end is threaded with 1" S.A.E. standard threads and carries a closure plug seating on a conical shoulder at the inner end of the threads. This plug is fitted with a standard male tubing connection at its outer end to fit a valve. A 1/8" hole bored through the plug serves as a gas passage. The closed end of the pipette is machined to a standard male tubing connection to fit a valve. A 1/8" hole bored through this connection to the inside of the pipette serves as a gas passage.

The position and design of this pipette has been shown by experience to be somewhat unsatisfactory by introducing ambiguity in the results. Another pipette of greater diameter and less length, and occupying a vertical position will be used in future work.

The construction of the liquid pipette is like that of the gas pipette except in its dimensions and the upper valve. In this case, the valve is of a right angle type, while the others are of the straight through types. An adapter connects the valve at the bottom of the liquid pipette to the copper tube, connecting to the discharge from the liquid pump. A tin container soldered around the upper end of the liquid pipette (Figure 7) is used to hold a freezing mixture at one point in the procedure.

The volumes of the gas and liquid sample pipettes were determined by weighing the amount of mercury required to fill them at 25°C. Computations showed that the variation in volume with pressure was insignificant, a result found experimentally in a similar case by Johnson (12). The variation in volume with temperature, computed from the coefficient of the thermal expansion of the steel used, is appreciable however. The following volumes in ccm. were found:

Temperature °C	25	60	98
Liquid Sample Pipette	59.72	59.79	59.87
Gas Sample Pipette	27.98	28.02	28.06

The measured volumes at 25°C are correct to ±0.04% as shown by three separate measurements as described.

The apparatus was designed to permit the use of a wide range of gas/oil ratios. As described it can be used only for rather high ratios and provision was made for experiments at lower ratios.

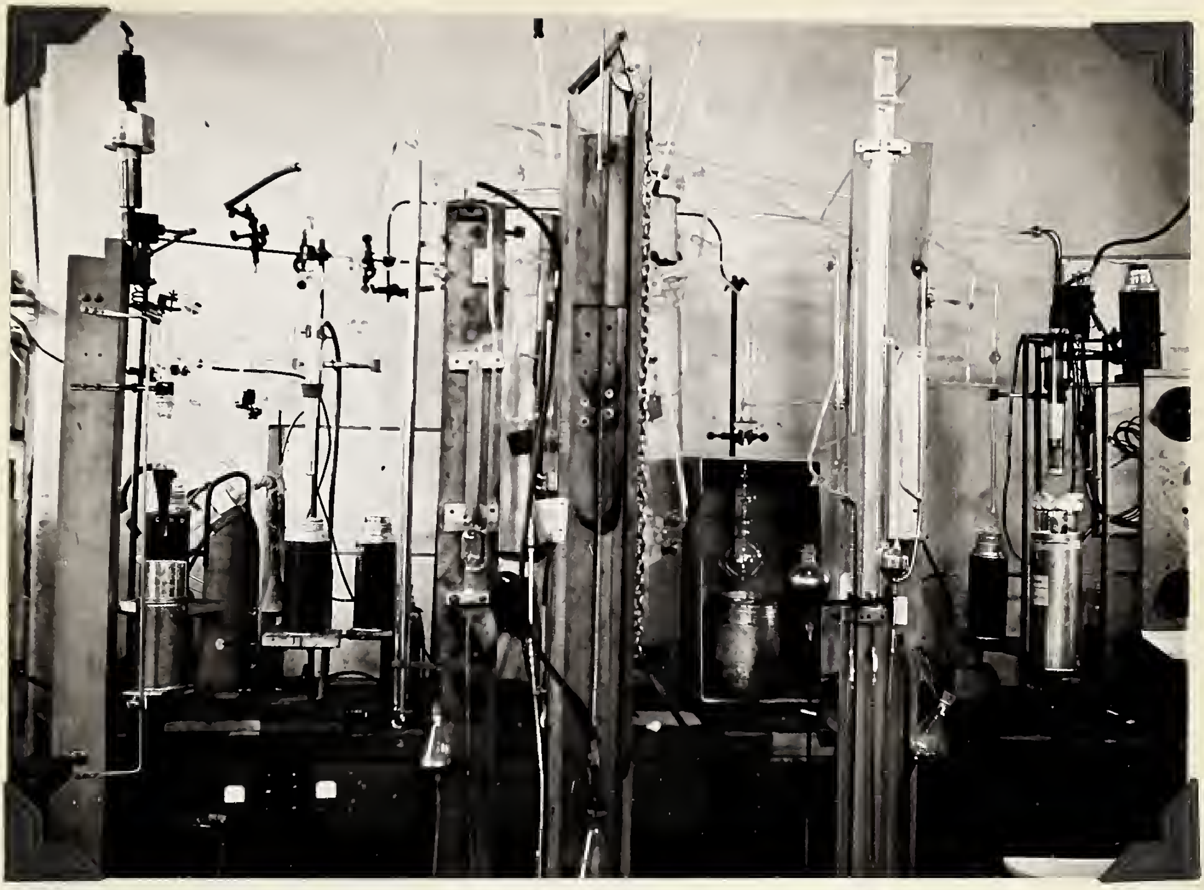


FIGURE 10 - The Analytical System.

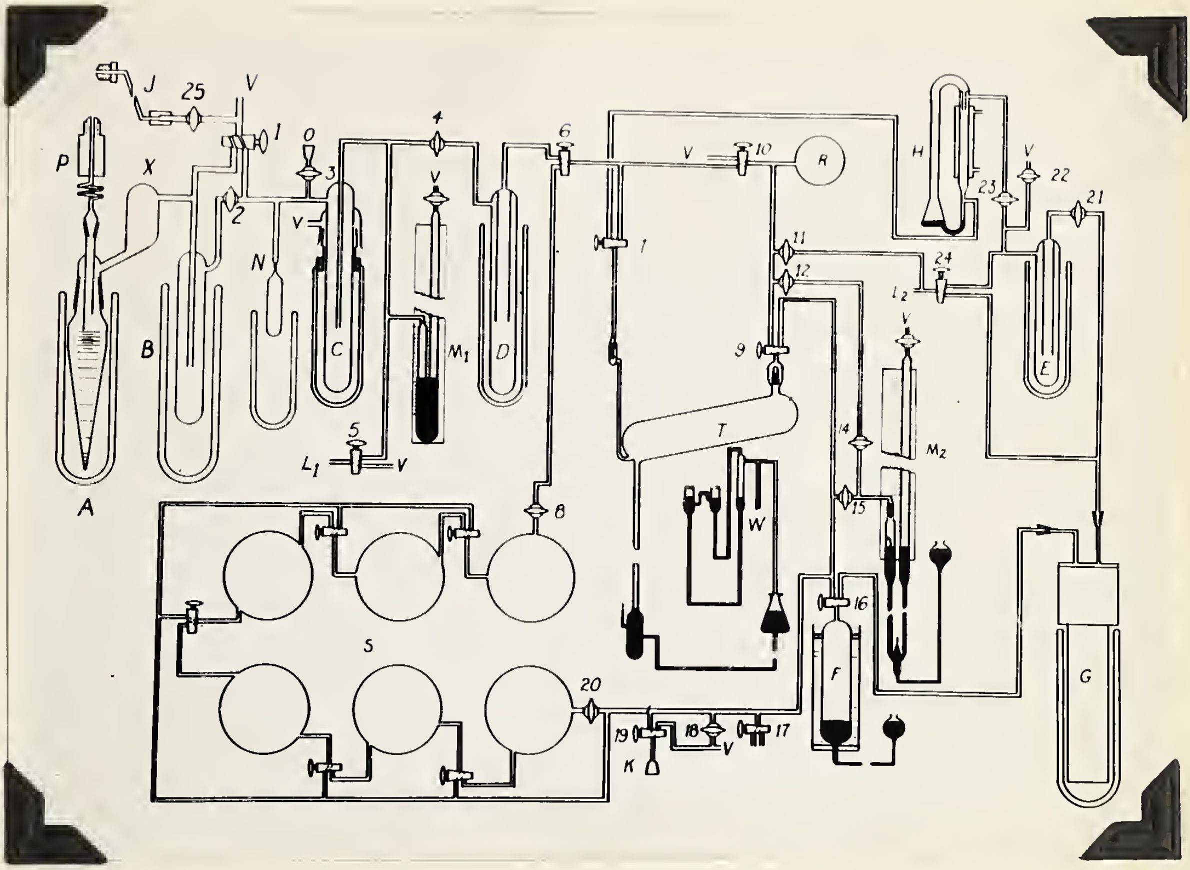


FIGURE 11 - Diagram of the Analytical System.

For the present series of experiments, a steel plug 5" long and 2 15/16" in diameter was placed in the cylinder between the pumps and the opposite end plate. This plug not only reduced the quantity of materials used in an experiment, an important consideration, but also permitted the use of lower gas/oil ratios. A second plug, 5" long, but only a half cylinder of 2 15/16" diameter in cross-section was also made. It may be fitted into the cylinder occupying gas phase space only and allowing still further reduced gas/oil ratios.

The analytical system is similar to that used by Gillies and Hugill (8). It is proposed to detail only changes in the apparatus, which were found necessary for the present work.

The apparatus is shown diagrammatically in Figure 11. It is composed of three parts, - the condenser train, the gas storage and measuring system, and the low temperature fractionation assembly. The apparatus is made of Pyrex glass throughout, except for special metal parts, and is designed for high vacuum work. The pumping system consists of a two stage mercury diffusion pump, backed by a Hyvac oil pump. A glass vacuum line is connected at suitable points, V, to the apparatus.

The gas sample and liquid sample pipettes are attached at connector P. To P is soldered a small bore, brass tube, coiled in a spiral, terminating in a standard taper, steel connection. To this connection, a ground glass joint is sealed, with sealing compound. Condenser A is connected to the apparatus by means of a ground glass joint. Trap X is necessary

to prevent liquid from condenser A being carried over mechanically into condenser B. Around condenser B is placed a Dewar Flask containing a dry ice-acetone mixture. Condenser C is sealed in a short outer tube carrying a vacuum connection and terminating in a ground joint which fits a ground joint inserted in the stopper of a Dewar Flask. This Dewar flask is filled with dry ice acetone mixture which under vacuum gives a temperature of -112°C. Condensers B and C are provided with double junction copper-constantan thermocouples. N is a small tube of about 5 ccm capacity, which is joined to the apparatus through a thin walled capillary tube. The fractions, condensed in condensers B and C, from the expansion of the gas phase sample, are distilled into N at the temperature of liquid air. N is removed from the apparatus by sealing off the capillary with an oxygen-gas flame.

The equilibrium cylinder may be connected to the vacuum line V through stopcock 25 by means of the copper tube J and a standard connector. The copper tube is soldered into one end of a brass cylinder. The glass tube is fitted into the other end, and sealed in place by means of sealing wax.

The entire measuring system is calibrated, and consists of six one-litre flasks mounted within an air bath. The system is connected to the Toepler pump T and the constant volume manometer M_2. The manometer scale was compared with a precision cathetometer and found to be without significant error.

The low temperature fractionation assembly has been fully described by Gillies and Hugill (8) and will not be discussed here. Description of a new portable gas analysis apparatus is given in Appendix I of this thesis.

The crude oil used in this work is stored over water in and dispensed from carboy A (Figure 3). An oil sample may be withdrawn at D, by opening stopcock 2, and raising the water resevoir B. The oil is dried over anhydrous calcium chloride in C. Drier C is connected to the assembly by means of two ground glass joints, permitting easy removal of the calcium chloride. The crude oil sampler consists of a one litre flask F, and capillary tubing, as shown in the diagram. The ground glass joint E fits the standard taper male connection on the equilibrium cylinder charging valve. Connection from the gas measuring pipette is made at H. All stopcocks and ground glass connections in the oil dispensing system are lubricated by a gel of mannitol and glycerol. This lubricant is insoluble in hydrocarbon oils and behaves satisfactorily if renewed frequently.

Procedure

1. P-V-T Relationships

The gas sample pipette V (Figure 6) was evacuated, and suspended in the large oil bath. Connection between valve 9 and the gas measuring pipette M, was made by a length of steel

tubing. The temperatures of the oil baths were adjusted to the desired values, and the high pressure gas handling system heated to about 60°C as described previously. Valves 2,4,5,6 and 9 were opened, and gas from storage admitted to the booster compressor D, at C. The pressure in the system was raised to the desired level, as indicated by the Bourdon gage F. The booster compressor was turned off, and valves 2,4 and 5 closed. The deadweight piston gage A was opened to the pipette, by opening valve 1. Fine adjustment of the pressure to the desired value was obtained by allowing gas to escape through valve 7, or by pumping mercury into the gas measuring pipette through valve 8. When the deadweight gage was balanced, valve 9, and then valves 1 and 6 were closed. The pipette V was removed from the oil bath and connected at P (Figure 11).

All necessary parts of the analytical and storage system were evacuated. The valve on the pipette was slightly opened and the gas allowed to expand through the Toepler pump T to the measuring flasks. The gas left in the pipette and condenser train was transferred by means of the Toepler pump to the measuring system, until the residual pressure, as measured by McLeod gage L_1, was about 1mm of mercury. The Toepler pump was then isolated, and the residual pressure measured exactly on the McLeod gage. The temperature of the storage bulbs was brought to constant value, by forced circulation of air in the cabinet. At this point, the pressure of the gas was measured on mano-

meter M_2 and the temperature of the bulbs noted. The temperature of the manometer was read.

Duplicate density measurements were made on the gas, using the calibrated density bulb attached at K. The technique used was that described by Gillies and Hugill (8).

Sample Calculation

The pressure-volume product of the compressed gas at pressure P and temperature T was calculated as follows:-

$$(PV) = \frac{(P_W - P_A) \times V_b}{14.696} \text{ ccm atmos.}$$

where P_W = Pressure reading at dead weight gage in p.s.i.

P_A = Atmospheric pressure p.s.i.

V_b = Volume of gas pipette in ccm.

The pressure-volume product of the expanded gas at 25°C and 76cm. of Hg. was calculated:-

$$(P_1V_1)^1 = \frac{Pm\left\{V_s + \frac{(V_r - V\ ) \times P_{McL}}{Pm}\right\}}{76} \times \frac{298.1}{T} \text{ ccm.atmos.}$$

where $(P_1V_1)^1$ = PV product using the ideal law.

Pm = Pressure at manometer in cm of Hg at 0°C

V_s = Volume of storage system

V_r = Volume of condenser train

P_{McL} = Pressure at McLeod gage in cm of Hg.

T = Absolute temperature of measuring flasks (room temperature)

$$\frac{(P_1V_1)}{(P_1V_1)^1} = 1 - \lambda$$

$$= 1 - b\Delta P$$

where (P_1V_1) = corrected PV product at 25°C and 76cm of Hg.

λ = deviation factor for gas at 1 atm. pressure.

b = deviation factor /cm

ΔP = 76 - Pm.

$\frac{(PV)}{(P_1V_1)}$ is plotted against P in Figure 12

Solubility Measurements

The equilibrium cylinder was set in place, as shown in Figure 6. Valves 9, 11, 12 and 13 were opened. The steel closure plug was removed from the standard taper connection T, and ground glass joint E (Figure 3) fitted over the connection. Stopcock I (Figure 3) was closed to the cylinder, and H connected to the gas measuring pipette at valve 6 (Figure 6) by means of rubber tubing. R was connected to the vacuum line, V, by the copper connection J (Figure 11). When the cylinder and pipettes were evacuated valve 10 was closed.

A sample of oil was drawn from storage into flask F (Figure 3), chilled in ice. The flask and the sample of oil were weighed, and flask F, put in place as shown in Figure 3, Stopcock I was opened, so that the oil from the flask entered the equilibrium cylinder at E. When nearly all the oil was drawn into the cylinder, stopcock I was turned so that H was connected to E. Valve 6 on the gas measuring pipette was opened, until the pressure in the equilibrium cylinder was atmospheric, as indicated by a manometer, connected at H (Figure 3). The amount of gas added was noted. The liquid sampler was disconnected and the closure plug, screwed quickly into the taper

connection T. The flask and residual oil were weighed, and the weight and volume of oil added was determined.

The volume of gas at 25°C and 1 atmosphere pressure, to give a desired gas/oil ratio was then calculated. From the PV - P curves (Figure 12) this volume was converted to the volume of gas at 60°C, the temperature of the gas measuring pipette, and at a reference pressure usually 1500 p.s.i.

Connection between the gas measuring pipette and the equilibrium cylinder was made by a length of steel tubing. Valve 10 was closed and valve 6 opened. Mercury in the gas measuring pipette was drained out through valve 7. The pressure of the gas in the pipette was raised to 1500 p.s.i., as measured by the deadweight gage. Valve 5 was closed and valve 10 opened and closed. Mercury was pumped into the pipette until the pressure was again 1500 p.s.i. This procedure was repeated until nearly all the gas in the measuring pipette had been added. The actual volume of gas added at 60°C and 1500 p.s.i. was determined by drawing off the mercury through valve 7 and weighing it. This technique was repeated until the required volume of gas had been added.

Valve 6 was then closed, and valves 1 and 10 opened. The drive mechanism of the pumps was started and the temperature of the oil bath adjusted to the desired level. The pumps in the equilibrium cylinder were operated until a constant pressure as indicated by the deadweight gage was reached. Generally

this took two hours.

At this point, valves I and 10 were closed, and the drive mechanism of the pumps stopped. The equilibrium cylinder was raised rapidly from the oil bath, and valves 9, 11, 12 and 13 closed. The pressure in the cylinder was released, and the gas pipette and the liquid pipette disconnected from the assembly.

Expansion of Gas Phase Sample

The gas pipette was attached at P (Figure 11), and all necessary parts of the analytical apparatus evacuated. Freezing mixtures of dry ice and acetone in Dewar flasks were placed around condensers B and C. The Dewar flask around condenser C was put on vacuum. When the temperatures of condensers B and C were -79°C and -112°C, respectively, the phase sample was expanded into the apparatus. The expansion was carried out slowly so that pentanes and heavier fractions were trapped in condensers B and C. The butanes and lighter left in the condenser train were pumped into the storage system by means of the Toepler pump T. The pressure in the train was reduced to 0.1 mm. by surrounding condenser D with liquid air. This procedure resulted in complete removal of the butanes and lighter gases from the condenser train with a minimum of pentanes and heavier hydrocarbons. Stopcock 4 was closed and the liquid air removed from condenser D. The gas produced upon evaporation of the liquid in condenser D was transferred completely to the measuring system. The gas was circulated automatically for 1

hour by means of a Maass control (19), connected to the water pump at W. The circulating system consisted of the measuring flasks and line to the manometer, Toepler pump, and the line from flask number I to the intake of the pump. The gas was measured, and duplicate density determinations were made. Duplicate samples were retained for analysis in the low temperature fractionation assembly.

Liquid air was placed around tube N, and the fractions from condensers B and C distilled into it. The tube was removed, by sealing off the capillary with an oxygen-gas flame. The weight of the fraction, and its refractive index were determined.

Expansion of Liquid Phase Sample

The expansion of the liquid phase sample was carried out in a similar manner. The greater portion of the oil was retained in condenser A, at room temperature. While the last of the butanes and lighter fractions were being removed from the condenser train, the oil in condenser A was agitated by a magnetic stirrer, operated from the outside by motion of a solenoid. The stirrer was constructed by sealing a piece of soft iron in a glass tube. This prevented the gas from being liberated in bursts from the oil with consequent movement to condenser B. The butanes and lighter fraction were treated as in the case of the gas phase sample.

When the pressure in the condenser train was 0.1 mm., and

with stopcock 4 closed, a freezing mixture of dry ice and acetone was placed in the cup soldered to the liquid sample pipette. The freezing mixtures were lowered from condensers B and C, and the light fractions therein distilled into the pipette. This procedure, repeated three to four times, served to wash down any oil residue left on the walls of the pipette. Finally, liquid air was placed around condenser A, and all the fractions distilled into it. Condenser A was removed and fitted with a cap, having a ground glass joint. The weight of the oil was determined and its density at 20°C measured. The mean molecular weight was determined by the cryoscopic method described by Gillies and Hugill (8). A sample of the oil was fractionally distilled using the fractionation column shown in Figure 4. The refractive index of each fraction was determined with a Pulfrich refractometer.

RESULTS AND DISCUSSION

The experimental results and their discussion will be presented in two principal parts. First will be given the P-V-T relationships of natural gas from Alberta Oil Incomes Well #2 (A.O.I. #2), plus a comparison with the behavior of somewhat similar gases (8) (27). Second, the behavior of the whole product of Alberta Oil Incomes Well #2 as a gas-liquid, two phase system in equilibrium will be presented.

P-V-T Relationships of A.O.I. #2 Gas

To obtain complete information as to the behavior of the natural gas used in this work, and as a matter of interest to know the fugacity and other properties of the gas as a function of pressure, its P-V-T relationships were determined at three temperatures, 25°C, 60°C and 98°C, and at pressures up to 200 atmospheres. (Table I).

The experimental procedure followed in determining the values of PV/P_1V_1 for pressures above one atmosphere has been described in detail previously.

In all tabled values of this ratio, P_1V_1 is the pressure volume product at 1 atm. and 25°C, i.e. 298.1°K, unless otherwise shown by a subscript giving another temperature. In order to convert these ratios into specific values of PV applicable to a unit mass of gas, the density or molecular weight of the

Table 1

Alberta Oil Incomes #2 Natural Gas

Experimental PV/P_1V_1 as a Function of Pressure at 25°C., 60°C., 98°C.

P	25°C	60°C	98°C
17.94	0.9502	1.0838	1.2243
	0.9514	1.0835	1.2245
34.95	0.9025	1.0482	1.1990
	0.9016	1.0468	1.2009
68.05	0.8084	0.9852	1.1566
	0.8085	0.9844	1.1571
102.99	0.7316	0.9363	1.1234
	0.7317	0.9349	1.1235
137.02	0.6977	0.9055	1.1017
	0.7014	0.9049	1.1030
171.04		0.8943	1.0967
		0.8943	1.0981
198.26			1.1066
			1.1059
205.06		0.9085	
		0.9108	

gas must be known for some particular conditions.

A large number of density determinations were carried out, at or near 25°C and 60 cm. of mercury pressure, in the usual manner employing a half litre glass flask and similar counterpoise. The average value obtained from some fifty determinations was 6.535×10^{-4} gr./ccm. at 25°C and 60 cm. of mercury pressure. The average deviation from the mean was 01.5%, a deviation much greater than was expected. In spite of many efforts to find the trouble, the deviation is still inexplicable, and is attributed provisionally to small variations in the content of the higher hydrocarbons in the gas.

The chemical composition of the gas, as determined by analysis, offers another means of obtaining a specific value of PV. The results of analysis of the A.O.I. #2 gas, using fractional distillation method already described, (See Table 6) give a molecular weight of 20.33 grams. The quantities of each component in the gas were measured at relatively low pressures, 30 cm. of mercury or less, and may be assumed to give an ideal result. Hence 20.33 grams is the true molecular weight. The density value given above, on the assumption of an ideal gas, gives a molecular weight of 20.252 grams. However, no comparison can be made without first considering the deviation from ideality of the gas at pressures below 1 atm.

There are two methods applicable to determinations of deviations at low pressures. First, a definite mass of gas

may be expanded at constant temperature to a succession of larger volumes and lower pressures. This was carried out using the system of measuring flasks and the precision manometer (Figure 11). The results showed the pressure volume product to vary linearly with pressure, increasing as the pressure decreased. This is in agreement with results of similar measurements by Jessen and Lightfoot (11). However, the slope of the line, measuring the deviation, was small and showed variations in successive experiments comparable in magnitude to the effect sought. Without a much more complex and precise apparatus, the experiments only show that the gas departs significantly from ideal behavior, at pressures below 1 atm.

The second method makes use of the plot of PV/P_1V_1 at pressures above 1 atm. As is widely recognized for gases relatively far removed from their critical temperature, PV/P_1V_1 varies linearly with pressure up to fairly high pressures, in this case to 40 atm. Extrapolation of PV/P_1V_1 curve from 40 atm. through 1 atm. to zero pressure gave results of more precision than was possible by means of low pressure expansions described. The value of PV per gram at 25°Cand 60 cm. of mercury pressure, computed from the density, was used as a reference point. From the slope of the PV/P_1V_1 vs. P line through this point, the value of P_1V_1, i.e. the pressure volume product at 1 atm. and 25°C, was computed to be 1207.28 ccm. atm. per gram. The deviation from ideality expressed as a residual volume is given by:

$$a = \frac{(P_0V_0/P_1V_1) - (PV/P_1V_1)}{P - P_0} \times P_1V_1$$

The higher accuracy obtained with the method using the slope of the high pressure PV/P_1V_1 line resulted from the different magnitudes of pressure range used in the two cases. In both cases, volumes were measured to an accuracy of 0.05 to 0.1% before and after expansions. However, the pressure change, appearing as the divisor in the expression for slope, was about 0.5 atm. in the low pressure expansions and 40 atm. in the high pressure expansions. The former pressure difference was measured to about 1 in 1500, and the latter to 1 in 6000. Evidently, on this basis alone, the slope as determined from high pressure expansions will be relatively much more accurate. Moreover, since the errors in pressure also appear in the PV products, whose difference appears as dividend, the relative accuracy of the high pressure expansions is further enhanced. The average relative error in the two methods will differ by a ratio of 15 or 20 to 1.

Using the PV/P_1V_1 vs. P line and extrapolating to zero pressure, a value of 1210.78 ccm. atm./gr. is obtained for P_0V_0 at 25°C. This latter value gives an ideal molecular weight of 20.215 grams, as compared to that of 20.33 computed from analysis. The discrepancy is greater than can be accounted for. As was pointed out before, the higher hydrocarbons may be the source of trouble in affecting either the density measurements, on which the value 20.215 is based, or the gas analysis. An error of 0.1 in the value for pentanes plus

the analysis will account for the difference. However, experience has not shown errors greater than 0.03 in such measurements.

For practical purposes, as in engineering applications, the discrepancy is of no account. For the purposes of this thesis, the density value will be used as reference.

In what follows all PV/P_1V_1 ratios will use the value for P_1V_1 at 25°C, i.e. 1207.28 ccm. atm./gr. as a reference. Ratios at other temperatures will be expressed as $(PV)_T/(P_1V_1)_{25}$.

Turning to the values of $(PV)_T/(P_1V_1)_{25}$ at 60°C and 98°C, it is necessary to determine the specific value of PV at some pressure and at these temperatures. Three methods are available. First, the variation of pressure with temperature for a definite mass of gas at constant volume may be determined, or second, the value of P_0V_0 at 25°C may be converted by the ideal gas law to give P_0V_0 at 60°C and at 98°C. Third, the slope of the $(PV)_T/(P_1V_1)_{25}$ line may be used in conjunction with the accepted value of $(P_1V_1)_{25}$.

Pressure-temperature measurements were made on about 500 ccm. of the gas at approximately 1 atm. pressure over the range 25 to 98°C. The relation between P and T was very nearly linear. In two experiments the following data were obtained:

T°C	I P	II P cm. of mercury
20	55.70	55.08
100	71.04	70.25
dP/dT	0.19175	0.18963
$=(1/P)(dP/dT)_{20^\circ C}$	0.0034425	0.0034428

The value of α may be compared with the ideal value at

20°C of 0.0034118.

The error in the above measurements is not significant in relation to density measurements, and the results can be used to compute densities at 60°C and 98°C or at other temperatures in this range from the experimental value at 25°C. However, the data is not precise enough for the computation of the deviations of the gas from ideality at pressures below 1 atm. Here, as previously, recourse is had to the third method with the second method as a check. The deviations at 60°C and 98°C were computed from the slope of the $(PV)_T/(P_1V_1)_{25}$ lines below 40 atm. pressure. The value of the ratio at zero pressure and the accepted value of $(P_1V_1)_{25}$ gave $(P_oV_o)_T$. The slope of the line, expressed as a residual volume subtracted from $(P_oV_o)_T$, gave $(P_1V_1)_T$. The values of P_oV_o at 60 and 98°C were calculated also from the value of P_oV_o at 25°C and the ideal gas law. This is justified by the fundamental theorem that Boyle's and Charles' laws apply exactly to gases at zero pressure. These values of P_oV_o were compared to P_oV_o values determined as above. The values of P_oV_o by the two methods agreed to better than 0.1%. The results based upon the former calculation are:

	25°C	60°C	98°C	
P_oV_o	1210.78	1353.48	1508.26	ccm. atm./gr.
P_1V_1	1207.28	1350.94	1506.59	" " "
a	3.497	2.538	1.675	ccm./gr.
K	4.0618	4.0640	4.0644	

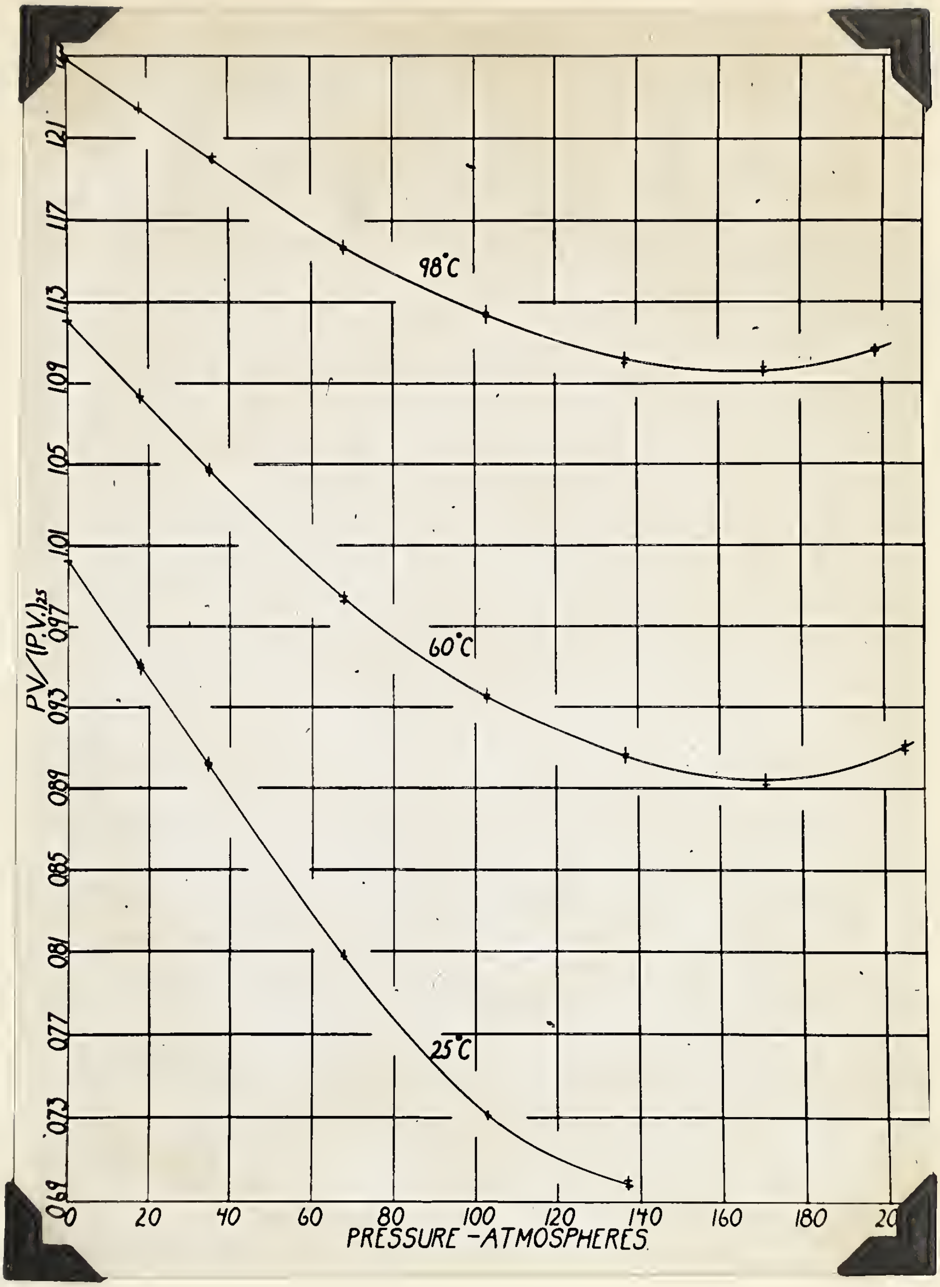


FIGURE 12 - The P-V-T Relationships of Alberta Oil Incomes #2 Natural Gas.

$$a = \text{Residual volume} = \frac{KT}{P} - V = \frac{P_0V_0}{P} - V$$

K = gas constant for 1 gram of gas.

The values for P_0V_0 at 60 and 98°C using the ideal gas laws and the value at 25°C are 1352.93 and 1507.28 respectively. The more direct experimental values tabled will be used in this thesis. It is for this reason that the anomalous result, a variation in K, is obtained. The absolute values of P_0V_0 and P_1V_1 are certainly correct to 1 ccm., and probably better, an accuracy within experimental error. The relative values of P_0V_0 and P_1V_1 at any temperature, as determined by the slope of the PV/P_1V_1 vs. P line, are much more accurate and their difference, namely 'a', is probably correct to 0.01 ccm.

The experimental values of $(PV)_T/(P_1V_1)_{25}$ as a function of pressure at three temperatures are given in Table 1. A large scale plot of these data, Figure 12, was made and the best curve drawn through the experimental points. Smoothed values taken from this curve are given in Table 2. Data on Royalite #27 gas obtained by Gillies and Hugill(8) were recalculated using improved values of constants, and the better methods developed in the present work. These data were also plotted, and the smoothed values for two temperatures are given in Table 2.

Evidently, both natural gases are similar in their behavior, the A.O.I. #2 gas deviating slightly more from ideality than the Royalite #27 gas. This could be predicted of course

Table 2

Smoothed Values of PV/P_1V_1 from Curves through Experimental Points

	25°C		60°C		98°C
P	A.O.I. #2	Royalite #27	A.O.I. #2	Royalite #27	A.O.I. #2
0	1.00290	1.00265	1.1211	1.1204	1.2493
1	1.0000	1.0000	1.1190	1.1184	1.2479
20	0.9450	0.9469	1.0789	1.0811	1.2216
40	0.8871	0.8966	1.0379	1.0427	1.1938
60	0.8300	0.8442	0.9991	1.0078	1.1669
80	0.7777	0.7983	0.9660	0.9771	1.1440
100	0.7363	0.7598	0.9393	0.9513	1.1258
120	0.7117	0.7319	0.9175	0.9317	1.1113
140	0.6982	0.7154	0.9033	0.9210	1.1012
160			0.8954	0.9168	1.0968
180			0.8953	0.9191	1.0994
200			0.9052	0.9279	1.1073

from the higher content of heavy hydrocarbons in the first gas. The deviation of a gas from ideality may be expressed by a deviation factor, according to the following relation:

$$\frac{P_oV_o}{P_1V_1} = 1 + \lambda$$

$$= 1 - b\Delta P$$

where λ = deviation factor

b = deviation factor per cm.

This relation is justified by the linear nature of the PV/P_1V_1 vs. P lines below 1 atm. pressure. The deviation factors for three gases at 25°C are given as follows:

Gas	λ	b (P in cm.Hg)	'a', ccm/gr.
A.O.L. #2	0.00290	0.0000382	3.497
Royalite #27	0.00265	0.0000349	3.316
Dominguez	0.00243	0.0000320	3.001

(See Table 4)

The course of the PV/P_1V_1 curves follows that predicted by van der Waals' equation of state. It is evident that the pressure of minimum PV/P_1V_1 ratio follows, with changing temperature, a parabolic path.

The value of PV at any pressure and temperature within the range of the experiments may be obtained from large scale plots. It is only necessary to estimate the $(PV)_T/(P_1V_1)_{25}$ ratio and multiply by $(P_1V_1)_{25}$ as given previously. The values of V, i.e. specific volume, or its reciprocal, density, may be obtained in turn by computation of $(PV)_T/P$.

The P-V-T relationships of these gases may be used directly in computing mechanical properties, and when expressed as

equations of state, lead to information regarding molecular forces and sizes, and the behavior of gas mixtures. The data may also be used to compute the thermodynamic properties of the gases, but generally only with considerable inconvenience. Even with an ideal gas, computation of thermal properties, excepting only free energy or work content, involves knowledge of such coefficients as dV/dT and d^2V/dT^2. The slopes of the curves such as V vs. T are very slight and accurate determination of the coefficients is almost impossible. Commonly, recourse is had to the well known device of using the variation of a residual rather than the direct quantity itself. In dealing with the behavior of gases, the quantity used to express their deviation from the ideal state is commonly the residual volume. This is defined as:

$$a = \frac{KT}{P} - V$$

where K is the gas constant for 1 gram of gas.

Physically, 'a' is the difference per unit mass between the volume the gas would occupy if ideal at the pressure concerned, and the volume actually occupied by the gas. The variation in 'a' with pressure and temperature is very much greater than the variation of V. It becomes relatively simple to determine, either analytically or graphically, integrals involving 'a' or differential coefficients in which 'a' is a variable.

In Table 3 are presented the residual volumes 'a' in ccm./gr. for three somewhat similar gases, A.O.I. #2, Royalite #27 and Dominguez (27). The residual volume for Royalite

Table 3

Residual Volumes ccm./gm.

P	T	A.O.I. #2	Royalite #27 (8)	Dominguez (27)
	25°C			
1		3.497	3.316	3.001
20		3.497	3.315	3.001
40		3.496	3.313	3.001
60		3.479	3.301	2.986
80		3.399	3.193	2.853
100		3.219	3.035	2.686
120		2.930	2.820	2.535
140		2.627	2.564	2.339
	60°C			
1		2.538	2.449	2.435
20		2.538	2.449	2.435
40		2.511	2.426	2.392
60		2.455	2.344	2.230
80		2.341	2.238	2.010
100		2.195	2.113	1.788
120		2.048	1.964	1.573
140		1.878	1.780	1.365
160		1.703	1.590	1.157
180		1.514	1.397	0.941
200		1.303	1.202	0.716
	98°C			
1		1.675		
20		1.675		
40		1.675		
60		1.658		
80		1.589		
100		1.491		
120		1.389		
140		1.277		
160		1.151		
180		1.005		
200		0.857		

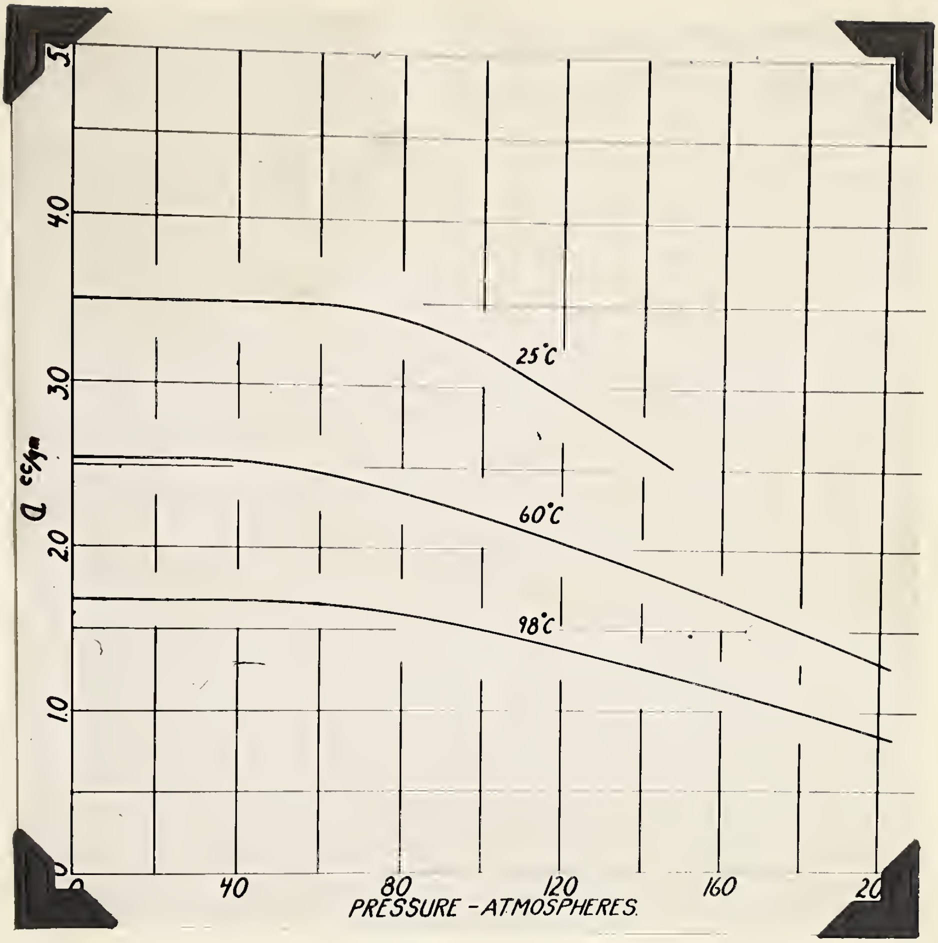


FIGURE 13 - The Variation of the "Residual Volume" with Pressure and Temperature.

#27 are those calculated from the corrected compressibility data for the gas presented in Table 2.

To determine PV at zero pressure for the Dominguez natural gas, it was assumed that the specific volumes reported (27) were obtained from measured densities and not calculated from the analyses. The value of PV at zero pressure for the $60^{o}C$ line, obtained by extrapolation of the compressibility data, is 1383.40 ccm. atm./gr. This may be compared to 1417.08 ccm.atm./gr. derived from the composition of the gas. This discrepancy is equivalent to an error of 0.5 grams in the molecular weight of the gas.

Molecular weight from analysis 19.291 gr.

Molecular weight from P-V-T data 19.761 gr.

These two values agree probably within the limit of error of the Podbelniak method of low temperature fractionation used to analyse the gas. The discrepancy is greater than that found in the present case of A.O.I. #2 gas discussed previously.

The residual volumes for A.O.I. #2 gas at $25^{o}C$, $60^{o}C$ and $98^{o}C$, as a function of pressure, are shown graphically in Figure 13. Similar curves may be obtained by plotting 'a' for Royalite #27 and Dominguez natural gas.

Inspection of the curves of 'a' vs. P for a particular temperature shows a trend from positive values through zero to negative values. The value of 'a' will become zero at the pressure corresponding to $-\ (P_oV_o)_T = (PV)_T$

The course of 'a' with changing pressure can be predicted by inspection of a suitable equation of state embodying both factors leading to deviations from ideality. Van der Waals' equation, while not of great precision, is simple and of the correct theoretical form. It is:

$$(P + A/V^2)(V - B) = Kt$$

rearranging

$$\frac{Kt}{P} - V = 'a' = A/PV - AB/PV^2 - B$$

Both A and B are small quantities and assumed, in this equation, to be constant. At low pressures, V is large and the term AB/PV^2 may be neglected. Furthermore, at low pressures the change in PV with pressure is small. Hence 'a' becomes equal to the quantity A/PV - B, that is almost constant, and as P approaches zero, approaches a finite constant value $A/P_oV_o - B$. This behavior is evident in Figure 13, where 'a' is constant within experimental error at pressures below 40 atm. Actually, PV varies appreciably in this range, but then A and B are not constants but vary with P in such a manner that the slope of the PV/P_1V_1 line is a constant below 40 atm. The data on 'a' may be used to evaluate the functions A and B at various temperatures and pressures. Upon expressing A and B as functions of T and P, a general, but highly complex equation of the Onnes type results.

As the pressure increases, and ignoring variations in A and B, the value of 'a' given by van der Waals' equation will begin to decrease. The change in the second term, AB/PV^2 is

much greater than that in A/PV or B and ultimately, the two negative terms predominate, 'a' becoming negative. The value of 'a' becomes zero at the pressure fixed by the relation:

$$A/PV = AB/PV^2 - B$$

The effect of temperature on 'a' may be predicted qualitatively by replacing PV by RT as a first approximation in ~~the~~ the expression for 'a'. Evidently, as the temperature is increased, 'a' will become less positive at low pressures and become negative at a lower pressure. Ultimately, at sufficiently high temperatures, 'a' will be negative at the lowest pressures and will become increasingly so as the pressure increases. The variation of 'a' with temperature at constant pressure may be used on extrapolation to give an approximate value of the temperature at which 'a' = 0 at P = 0, i.e., the Boyle Point.

On considering the expression of the deviation from ideal behavior shown by a real gas, in general two methods are available. It is always possible, as has been indicated, to express the P-V-T relationships analytically as an equation of state. For any wide pressure range such as that used in the present work, such equations are complex and their application in computing properties of the gas is difficult. Alternatively, the familiar and simple expressions such as the ideal gas laws and derivatives therefrom may be retained, except that, in place of pressures, a new variable is used that gives correct results. Such a variable is purely empirical in nature and defined

arbitrarily. Its justification lies only in its utility.

The second method above was first clearly proposed and expressed quantitatively by Lewis (18). The free energy of matter may be considered as a measure of the "escaping tendency". If the free energy of a substance is greater in one part of a system than in another, the substance will migrate from the former to the latter region. Stated generally, the requirement for equilibrium in a system is that the free energy i.e. the "escaping tendency" of a component is the same in all parts of a phase and in all phases. In the case of a gas, pressure is the direct measure of free energy in that it determines the work content and "escaping tendency" of the gas. If the gas obeys the ideal law, the relation between free energy and pressure takes the well known form:

$$F = Kt \ln p + F_0$$

where F_0 is the free energy of the gas at zero pressure and is a function of temperature only

K is the gas constant, proportional to the mass of gas under consideration. However, in the case where the gas is not ideal, no such simple expression is available. Lewis (18) introduced the quantity "fugacity" as a direct measure of escaping tendency by means of the definition:

$$F = Kt \ln f + F_0 \qquad 1.$$

Thus, a simple equation is retained. Between two isothermal states

$$\Delta F = Kt \ln f_1/f_2 \qquad 2.$$

For an ideal gas:

$f = p$ in the same units, and for a real gas:

$$f \rightarrow p \text{ as } p \rightarrow 0 \qquad 3.$$

The relation of fugacity to pressure may be derived as follows:

For infinitessimal isothermal changes,

$$dF = vdp$$

Combining this with 2. above,

$$(d \ln f/dp)_T = V/Kt$$

Rearranging and integrating,

$$Kt \ln f_1/f_2 = \int_{P_1}^{P_2} VdP$$

Introducing the residual volume, defined previously as

$$a = \frac{Kt}{P} - V$$

and the relation 3. above,

$$\ln f = \ln P - \frac{1}{Kt} \int_0^P adP \qquad 4.$$

The fugacities of the gases investigated in the present work were computed from equation 4.; evaluation of the integral being carried out graphically on a large scale plot of 'a' vs. P at each temperature. The values of fugacity for three gases are given as f_1 in Table 4, and shown graphically for the case of A.O.I. #2 gas in Figure 14.

The difference between fugacity and pressure, or alternatively, the ratio f/p (the activity coefficient), changes with pressure in a manner predictable from van der Waals' equation, or from the variation of 'a' with pressure. Up to pressures at which 'a' is positive, p/f increases, passes through a maximum and decreases while (p - f) always increases. An estimate of the pressure at which 'a' equals zero for A.O.I.

#2 gas at 25°C is 350 atm. Beyond the pressure at which 'a' becomes negative, both quantities decrease until at some pressure, $p/f = 1$ and $(p-f) = 0$. At this pressure, beyond the range of experiment here, the area enclosed by positive values of 'a', (Figure 13), equals the area enclosed by negative values of 'a'. Beyond this pressure, p/f is less than 1 and $(p - f)$ is negative, i.e. fugacity is greater than pressure. In this high pressure range, the physical interpretation compares the gas to a liquid; the mean free path has no meaning, the molecules are in contact, and the compressability is that of the molecules themselves. In terms of van der Waals' equation, the quantity B predominates.

The gases investigated are all mixtures and it is of interest, both theoretically and practically, to examine the relation between composition and pressure or fugacity. Dalton's law of partial pressures will not serve to compute the pressure of the mixture with any precision above a few atmospheres and needs no consideration. The discrepancies shown by Dalton's law are the same in relative magnitude as the departure of the ratio PV/P_1V_1 from a constant value. These have been discussed and are evident in Figure 12. Of other means of relating composition and pressure, the method known as "Lewis' Fugacity Rule" (18) only, will be examined. This rule, discussed previously, requires for its application a knowledge of the fugacity-pressure relationships for each of the components in the gas mixture. The fugacity data used were taken from the

Table 4

Fugacities

P	T	A.O.I. #2		Royalite #27		Dominguez	
		f_1	f_2	f_1	f_2	f_1	f_2
20	25°C	18.87	18.17	18.95	18.35	19.05	19.26
40		35.61	34.24	35.90	34.79	36.30	36.52
60		50.41	48.20	51.02	49.39	51.88	51.82
80		63.46	61.35	64.51	63.15	65.97	66.17
100		75.06	73.77	76.63	76.20	78.86	79.75
120		85.57	85.63	87.65	88.69	90.72	92.65
140		95.33	96.99	97.86	100.67	101.74	105.01
20	60°C	19.26	18.86	19.30	18.98	19.31	19.96
40		37.10	35.87	37.24	36.26	37.29	38.25
60		53.62	51.74	53.95	52.54	54.08	55.59
80		68.98	66.60	69.56	67.93	69.94	72.03
100		83.36	80.79	84.22	82.74	85.05	87.74
120		96.92	94.56	98.10	97.12	99.61	102.82
140		109.82	107.96	111.36	111.14	113.78	117.39
160		122.21	121.14	124.35	124.96	127.78	131.68
180		134.23	134.18	136.87	138.59	141.57	144.76
200		146.04	147.18	149.22	152.17	155.42	158.73
20	98°C	19.56	19.31				
40		38.25	37.16				
60		56.11	53.98				
80		73.20	70.59				
100		89.64	86.37				
120		105.50	101.77				
140		120.92	117.12				
160		135.98	132.01				
180		150.79	147.16				
200		165.48	161.98				

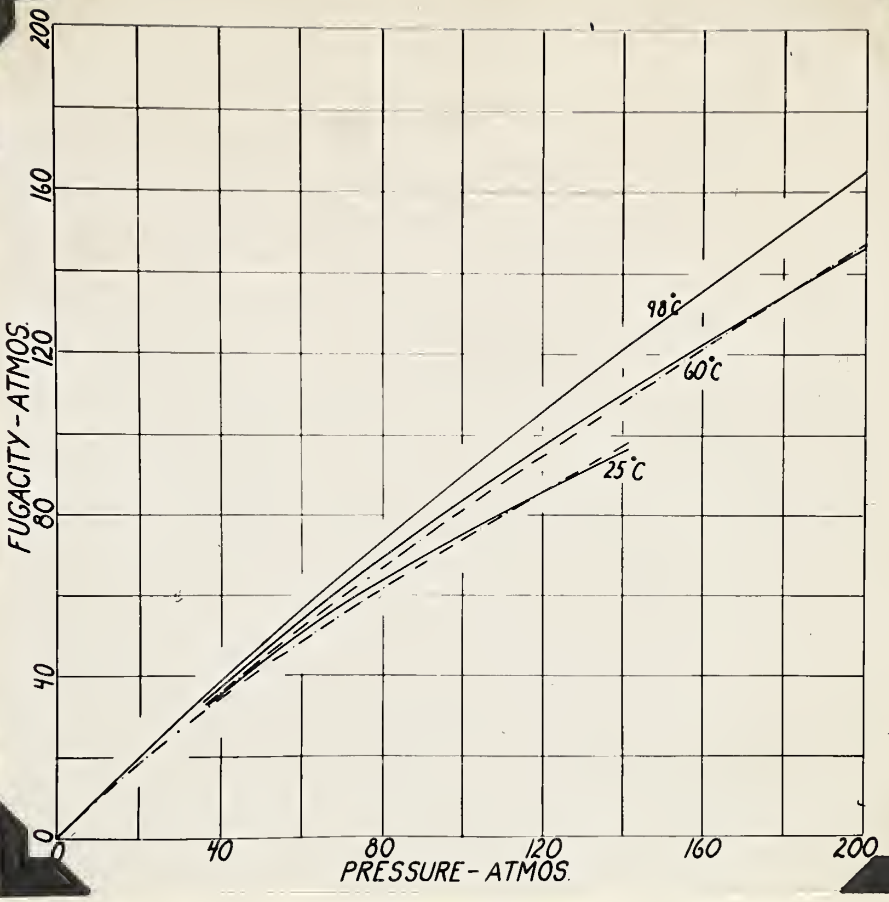


FIGURE 14 - The Fugacity of Alberta Oil Incomes #2
Natural Gas.

______ Fugacity from P-V-T Relationships.

_·_ _ _ Fugacity by Lewis' Rule.

literature and are shown, together with the sources, in Table 5. These data are considered the best available and are probably more accurate than Lewis' Rule. However, it must be borne in mind that errors in measurement, and possibly impurities in the gas may be present to limit the accuracy of the data.

The fugacities calculated by Lewis' Rule for the gases under investigation are given as f_2 in Table 4 and may be compared with the experimental values f_1. The calculated values for A.O.I. #2 gas are also shown graphically in Figure 14.

Evidently there is some merit in Lewis' Fugacity Rule. In most practical applications involving the use of the properties of a mixture of hydrocarbon gases, the fugacity as calculated by the rule is sufficiently exact. The use of the rule requires of course a knowledge of the fugactity-pressure relationships for each component of the mixture. This is not a serious disadvantage today, since the body of such information on pure gases is large and increasing. It is also true that in many cases the fugacity- pressure relationships of a pure substance may be predicted from a knowledge of the same relationships for similar or related compounds.

The principal use made of the fugacity-pressure relationships or what in practise is the same thing, the 'a' - p relationships, is in the calculation of thermal properties such as heat capacity, enthalpy, free energy, entropy, and Joule-Thomson coefficients as functions of temperature and pressure.

These computations involve the integration of well known differential equations of thermodynamics, and are generally

Table 5

Fugacities of Pure Components

P	CH_4(29)	C_2H_6(29)	C_3H_8(31)	C_4H_{10}(32)	C_5H_{12}(30)	N_2(3)	CO_2(18)
25°C							
20	19.31	17.01	8.44	2.45	0.75	19.94	*
40	37.31	28.65	9.02	2.65	0.82	39.77	
60	54.11	30.93	9.66	2.86	0.88	59.55	
80	69.86	33.07	10.34	3.13	0.99	79.38	
100	84.69	35.25	11.09	3.40	1.09	99.42	
120	98.78	37.56	11.84	3.67	1.18	120.0	
140	112.21	39.91	12.72	3.97	1.29	140.58	
160	125.18	42.39	13.55	4.29	1.43	161.16	
180	137.81	44.92	14.52	4.65	1.55	181.72	
200	150.34	47.36	15.51	5.02	1.69	202.30	
60°C							
20	19.55	18.01	15.33	5.85	2.16	20.02	19.2
40	38.27	32.04	16.99	6.33	2.36	40.11	35.3
60	56.22	42.06	18.13	6.85	2.56	60.31	49.5
80	73.47	48.12	19.50	7.40	2.82	80.68	61.1
100	90.15	52.61	20.86	7.98	3.07	101.14	70.4
120	106.31	56.51	22.25	8.61	3.36	122.66	76.6
140	122.02	60.49	23.91	9.29	3.66	144.18	81.2
160	137.44	64.41	25.53	10.01	4.00	165.70	85.0
180	152.66	68.41	27.23	10.79	4.36	187.22	88.2
200	167.78	72.61	29.03	11.62	4.74	208.8	91.0
98°C							
20	19.78	18.80	16.48	11.76	5.18	20.08	
40	38.80	34.85	25.97	12.78	5.58	40.35	
60	57.35	47.75	29.21	13.78	6.18	60.84	
80	75.95	58.82	31.61	14.80	6.70	81.59	
100	93.85	67.80	34.10	16.10	7.30	102.0	
120	111.45	75.30	36.55	17.41	7.85	124.3	
140	129.05	82.15	39.30	18.70	8.50	146.6	
160	146.15	88.55	42.15	20.00	9.35	168.8	
180	163.55	94.97	45.05	21.45	10.20	191.1	
200	180.55	101.35	47.90	23.00	10.98	213.5	

* For purposes of calculating the fugacity of Dominguez Natural Gas (27) at 25°C the fugacity of CO_2 at 25°C was assumed to be the same as the fugacity of C_2H_6 at 25°C.

Table 6

Gas Analyses

	A.O.I. #2	Royalite #27 (8)	Dominguez (27)
CH_4	78.39	79.57	87.78
C_2H_6	12.49	9.47	3.82
C_3H_8	4.59	4.03	3.36
C_4H_{10}	1.56	1.56	2.00
C_5H_{12}	0.54 (X)	0.37 (X)	0.64
$C_5H_{12}+$	---	---	0.30
N_2	2.42	5.00	1.50 (#)
CO_2	---	---	0.60

(#) $N_2 + O_2$

(X) C_5H_{12} and higher

Compositions are mol percent.

carried out by graphical methods using large scale plots of 'a', da/dT and d^2a/dT^2(6). Preliminary steps to this end have been taken in connection with the gases investigated but time has not permitted the completion of the multiplicity of computations involved.

Symbols

M_g - Mols of gas as butanes and lighter

M_p - Total mols in phase

(V_g) - Volume of gas, butanes and lighter, at t°C. and 1 atm.

V_o - Volume of oil, including pentanes and heavier, in same units as V_g

F_g - Cu.ft. of gas, butanes and lighter, at 20°C. and 1 atm.

Bbl.-35 Imperial gallons

M_o - Mols of oil, including pentanes and heavier

V_p - Volume of phase under equilibrium conditions, $(V_p)_g$ for gas phase; $(V_p)_l$ for liquid phase

G_o - Gallons of oil, pentanes and heavier, at 20°C.

F_p - Volume of phase under equilibrium conditions, in cu.ft.

X_p - Volume of phase when expanded to 1 atm. and 25°C.

K_1 - Ratio of mol fraction methane + nitrogen in gas phase to that in liquid phase

K_2, K_3, K_4 - Ratio of mol fractions as above for ethane, propane and butane

K_c - Ratio of mol fractions of light fraction i.e. $C_5H_{12}+$ in gas phase to mol fraction of same material, as determined by refractive index, in liquid phase

Equilibrium Measurements

The direct experimental data is presented in Table 7. The properties of the gas and liquid phases and of the system at equilibrium conditions are given in Table 8.

In the four determinations, the equilibrium cylinder was charged with gas and crude oil at a gas/oil ratio of 900 cu.ft., measured at 25°C and 76 cm. of mercury, per barrel, in the manner previously described. This was taken as a representative gas/oil ratio of the younger wells in the Turner Valley field. The gas referred to is A.O.I. #2 gas as treated and stored in the laboratory. In the expression for gas/oil ratios given in Table 8, the gas referred to is the mixture containing only butanes and lighter hydrocarbons. The charge of gas and crude oil was added with an error not greater than .1%. The determinations were carried out at only one temperature, 98°C, which is somewhat higher than the bottom hole temperature of the Alberta Oil Incomes #2 well, as of Dec. 28, 1940.

Experimental conditions were carefully controlled at all times. Temperatures were measured using calibrated thermometers. The experimental data of Run #I show some variations from the trend of the others. These deviations can be attributed probably to inexperience in the experimental technique. In only one determination, Run #5, were the producing conditions of the well proximated.

The liquid separated from the liquid phase sample was

Table No. 7

General Experimental Data

Liquid Phase Samples (59.87 ccm.) and
Gas Phase Samples (28.06 ccm.) at 98°C.

Run No.	1	2	4	5
Pressure, atm.	58.3	53.9	69.6	158.6
Oil, ccm. at 25°C.	247.0	232.7	282.3	536.5
Oil, grms.	199.4	187.9	228.0	433.2
Gas, ccm. at 25°C., 1 atm.	40380	36887	45809	85346
Gas, grms.	33.43	30.54	37.92	70.65

Liquid Phase Sample

Run No.	1	2	4	5
Liquid separated				
grms.	41.22	41.31	40.32	35.71
density, gr./ccm., 20°C.	.8203	.8203	.8192	.8160
volume, ccm., 20°C.	50.25	50.36	49.22	43.76
molecular weight	191.4	184.3	181.0	174.0
volume, light fraction, ccm.	8.21	8.08	8.99	6.10
weight, light fraction, grms.	5.84	5.75	6.38	4.29
Gas volume, ccm., 25°C., 1 atm.	2127.1	2000.0	2350.7	4849.7
Gas density, gr./litre, 25°C., 1 atm.	1.166	1.163	1.075	.9905
Gas mass, grms.	2.480	2.326	2.527	4.804
Composition of gas, mol %:				
$CH_4 + N_2$	53.99	53.47	59.82	69.95
C_2H_6	19.68	20.09	19.95	14.60
C_3H_8	15.11	15.93	13.13	9.05
C_4H_{10}	8.59	8.58	4.89	4.57
$C_5H_{12}+$	2.73	1.93	2.21	1.83

Gas Phase Sample

Run No.	1	2	4	5
Liquid separated				
grms.	.2393	.3256	.3164	.4830
refractive index	1.407	1.409	1.405	1.397
molecular weight	97.5	98	97	95
density, grms./ccm., 20°C.	.710	.711	.709	.703
Gas volume, ccm., 25°C., 1 atm.	1378.6	1259.5	1654.9	3911.2
Gas density, gr./litre, 25°C., 1 atm.	.8583	.8360	.8357	.7990
Gas mass, grms.	1.183	1.053	1.383	3.125
Composition of gas, mol %:				
$CH_4 + N_2$	81.80	82.46	83.28	86.45
C_2H_6	10.07	10.15	9.65	8.07
C_3H_8	4.16	4.28	3.90	3.16
C_4H_{10}	2.60	2.17	2.14	1.48
$C_5H_{12}+$	1.37	0.94	1.02	0.84

Table No. 8

Properties of Gas and Liquid Phases and of System at Equilibrium Conditions, 98°C.

Run No.	1	2	4	5
Pressure	58.3	53.9	69.6	158.6
Liquid Phase				
Volume, ccm., $(V_p)_1$	273.7	253.7	326.0	699.7
Mass, grms.	199.8	184.9	233.3	473.4
Density, grms./ccm.	.7299	.7289	.7157	.6766
Composition in mol fractions				
$CH_4 + N_2$	.1550	.1429	.1803	.3437
C_2H_6	.0566	.0537	.0601	.0717
C_3H_8	.0435	.0426	.0402	.0445
C_4H_{10}	.0247	.0229	.0143	.0225
Light fraction	.2059	.1967	.2127	.1209
Residue	.5143	.5412	.4924	.3967
M_g/M_p	.2798	.2621	.2949	.4824
$(V_g)_{20}/(V_p)_1$	33.98	32.21	27.76	78.19
$(V_g)_{20}/(V_o)_{20}$	40.27	38.15	45.70	105.95
F_g/bbl., $C_5H_{12}+$	226.3	214.4	256.8	595.3
Gas Phase				
Volume, ccm., $(V_p)_g$	662.7	682.7	610.4	236.7
Mass, grms.	33.61	33.54	32.61	30.44
Density, grms./ccm.	.05071	.04913	.05342	.1286
Composition in mol fractions				
$CH_4 + N_2$	.7839	.7747	.7945	.8379
C_2H_6	.0964	.0954	.0921	.0782
C_3H_8	.0399	.0401	.0372	.0306
C_4H_{10}	.0249	.0204	.0204	.0144
Light fraction $(C_5H_{12}+)$	.0549	.0694	.0558	.0389
$M_o/(V_p)_g$ in litres	.1151	.1354	.1411	.2288
$G_o/(F_p)_g$	.0984	.1164	.1202	.1926
G_o/X_p in 1000cu.ft. units	1.927	2.402	1.952	1.343
$X_p/(V_p)_g$ in same units	55.11	47.53	61.58	143.46
System Properties				
$(V_p)_g/(V_p)_1$	2.421	2.691	1.872	.3383
Equilibrium Constants				
K_1	5.058	5.421	4.407	2.438
K_2	1.703	1.777	1.533	1.091
K_3	.917	.941	.925	.688
K_4	1.003	.891	1.427	.640
K_c	.267	.353	.262	.322

weighed to 0.01 gms., and its density determined gravimetrically. The volume of the gas was measured in the analytical system, at 55 to 60 cm. of mercury pressure and 23 to 26°C. The volume was reduced to 25°C and 76 cm. of mercury, using the deviation factor determined in connection with measurements on the P-V-T behavior of M.O.I. #2 gas itself. The slight difference in composition between the gas from the equilibrium system and M.O.I. #2 gas is of no significance in the factor. The precision of the gas density measurements and the gas analyses has been discussed previously.

The weight of the light fraction condensed from the gas phase was determined using a sealed tube technique, which is much more accurate than the method used in a previous series of experiments (8). From its refractive index, the molecular weight and density of the light fraction were calculated using refractive index-molecular weight-density relationships of Sterling Pacific naphtha (23). This procedure introduces some uncertainty in these data. Until the molecular weight, density and refractive index relationship is established for the M.O.I. #2, oil, the data will serve as an approximation at least. The corresponding light fraction in the liquid phase was determined by fractional distillation of the liquid separated. The volume which had the same refractive index as the light fraction of the gas phase was assumed to be light fraction.

Approximately ½ ccm. of a heavier fraction was condensed from the gas phase sample at room temperature. This quantity has not been considered in the calculations because its weight was determined only in Runs #4 and #5, and further, its origin is somewhat obscure. An approximate weight balance computation on Run #5 showed that the difference between the weight of the liquid added and the weight of liquid at equilibrium conditions was 13 gms. Five grams of pentane and heavier, in excess of that added as gas, were found in the gas phase. This amounts to approximately 0.8 gm. in the gas phase sample. In Run #5, 0.39 gm. of heavier fraction were found, leaving a discrepancy of around 0.4 grams. This would indicate that the heavy fraction is present as vapor in the gas phase at equilibrium, not due to a mechanical defect in the procedure or equilibrium cylinder, leading to the entry of liquid as such to the gas sample pipette. A definite statement cannot be made until further experiments are carried out. If this heavy fraction is real, then the calculations of the properties of the gas phase are in error by more than 10%.

In previous work in this laboratory (23)(8), naphthas from the limestone zone gas cap were used. This naphtha, presumably present in the gas cap as vapor, showed a boiling range up to 150°C at atmospheric pressure. In February, 1936, a temperature of 70 to 75°F for this zone was recorded by the Petroleum and Natural Gas Conservation Board. Then in the

present instance at 98°C it is highly probable that even higher boiling fractions can exist as vapor in the gas phase.

Knowing the volume of the equilibrium cylinder and the molecular weights of the condensates, the total number of mols in the system was calculated. From the gas analyses, which within experimental error gives mol percent, the mol fractions of the lighter components were determined. These are presented in Table 8. The distribution of the lighter components is given by the equilibrium constants $K_1 - K_c$. The equilibrium constant is the ratio of the mol fraction of a component in the gas phase, to the mol fraction of the same component in the liquid phase. In the case of ideal gaseous and liquid solutions, these constants are independent of pressure and vary for a particular component with temperature only. In the case of methane plus nitrogen, and ethane, the equilibrium constants decrease with increase in pressure, as is customary in such systems. The change in the constant is explicable on consideration of the changing composition of the gas and the liquid phase with increasing pressure.

The equilibrium constants K_3, K_4 and K_c show no such regular trend, and are, within the limit of error, relatively much more constant. This suggests that in the pressure range used, the system goes through the region where the phenomenon of retrograde condensation becomes apparent for the lighter hydrocarbons. If this is so, a true picture of the phase equilibrium will not be obtained, until experiments at inter-

mediate pressures have been carried out.

From analysis of the phase samples, and determination of phase volumes, the phase densities and masses were calculated. Except for Run #I the liquid phase density decreases with increased pressure. This is due to solution of lighter components from the gas phase in the liquid phase, and transfer of pentanes and higher from the liquid phase to the gas phase as predicted by Poynting's equation.

The increase in density of the gas phase with pressure is a combination of three factors. First, the normal increase in density of the gas with pressure. Second, the solution of butanes and propanes in the liquid phase, reducing the density and third, the transfer of pentanes and higher hydrocarbons from the liquid phase to the gas phase. The first and third of these predominate.

The increased transfer of pentanes and higher hydrocarbons to the gas phase with pressure is shown in the derived data for the gas phase in Table 8. The compressibility of the gas phase is given by the ratio $X_p/(V_p)g$ i.e. the ratio of the volume of the expanded phase at $25^\circ C$ and 1 atm., to the volume of the phase under equilibrium conditions. Per unit volume of gas phase space, the content of pentanes plus increases with pressure. This is shown by the vapor content expressed as mols or gallons of condensible liquid in the ratios $M_o/(V_p)_g$ and $G_o/(F_p)_g$. However, the reverse is true in the case of the expanded phase, i.e. the content of condensible liquid per

unit volume of expanded gas decreases with increasing pressure. This is shown in the gallons of oil per 1000 cu.ft. of expanded phase at ordinary conditions given as C_o/X_p in Table 8. This is in contrast to the behavior of simple systems (12) and of complex systems (8) using more volatile liquid materials. It may be concluded that the effect of pressure on the vapor pressures of the less volatile hydrocarbons in A.O.I. #2 oil is too small to produce the phenomenon of retrograde condensation at the pressures used here.

The value of the data on the gas phase, in application to the field, lies principally in computation of the material content of any gas cap in the producing zone. The ratio, $X_p/(V_p)_g$ expresses the total quantity of material as gas, measured at ordinary conditions, contained in unit volume of free space in the producing formation. Given the porosity of the formation, it is possible from such data to compute the displacement in a formation yielding only gas. It should be pointed out that this does not imply that there is a gas phase in the limestone zone feeding A.O.I. #2 well.

Turning to the data on the liquid phase, the results are interesting in suggesting that the A.O.I. #2 well was fed, at the time of sampling by material substantially liquid. At a pressure of 158.6 atm. and at 98°C, the gas/oil ratio, Fg/bbl., was found in this work to be 595.3 cu.ft. of butanes and lighter gases at 20°C and 1 atm. per bbl. of oil. This ratio will increase, roughly, proportionally to the pressure. The well

was operating at the time of the sampling at a gas/oil ratio of 700 cu. ft./bbl. a value that will be reduced somewhat by taking into account the pentanes plus content of the gas. The last measurement of bottom hole temperature and pressure, 20 days previous to sampling, showed 92.2°C and 188 atm. Under these conditions, assuming equilibrium, the experiments show beyond doubt that a single liquid phase, possibly unsaturated, can account for the performance of the well.

Time has not permitted further experiments over a range of temperatures and other pressures. Until such work was been carried out, the conditions in the formation cannot be stated with certainty. Further, this additional information is necessary before estimates of the material content of the formation can be made. The values of density and composition given in Table 8 were obtained under conditions too far removed from actual well conditions to warrant extrapolation.

Finally, the significance of the ratio, $(V_p)_g/(V_p)_l$, a property of the system as a whole, should be pointed out. This ratio, the volume of the gas phase/the volume of the liquid phase, in situ, decreases regularly with increasing pressure. Though the gas/oil ratio of the system as a whole is constant, the total mass increases with pressure. As the pressure approaches the value at which the solubility of the gas in the oil becomes equal to 900 cu.ft./bbl. the ratio $(V_p)_g/(V_p)_l$ approaches zero. In other words, no gas phase can exist in the equilibrium system. It is possible that, given sufficient data at other

temperatures and pressures, the variation of this ratio may be used to determine most directly the phase conditions in the producing formation. It appears probable that if the system were put together at a gas/oil ratio of 700 cu. ft./bbl.and 92.2°C at a mass/volume ratio required to reach a pressure of 188 atm., there would exist only a single liquid phase. In terms of the present apparatus, the gas phase pipette would yield a liquid sample identical with the sample from the liquid phase pipette.

SUMMARY

The P-V-T relationships of Alberta Oil Incomes #2 gas have been studied at three temperatures, 25°C, 60°C and 98°C, over a pressure range from 15 cm. of mercury to 3000 p.s.i. The residual volumes and fugacities for this gas, and for two other natural gases, have been calculated. The fugacities of the three gases at 25°C and 60°C have been compared with the fugacities predicted by Lewis' fugacity rule.

A new apparatus for studying phase equilibrium in hydrocarbon systems has been described. The results of four equilibrium determinations have been presented. Various properties of both the liquid and the gas phases have been derived from the experimental data, and the nature of future work has been indicated.

A description of a portable apparatus for the analysis of hydrocarbon gases, has been given in Appendix I.

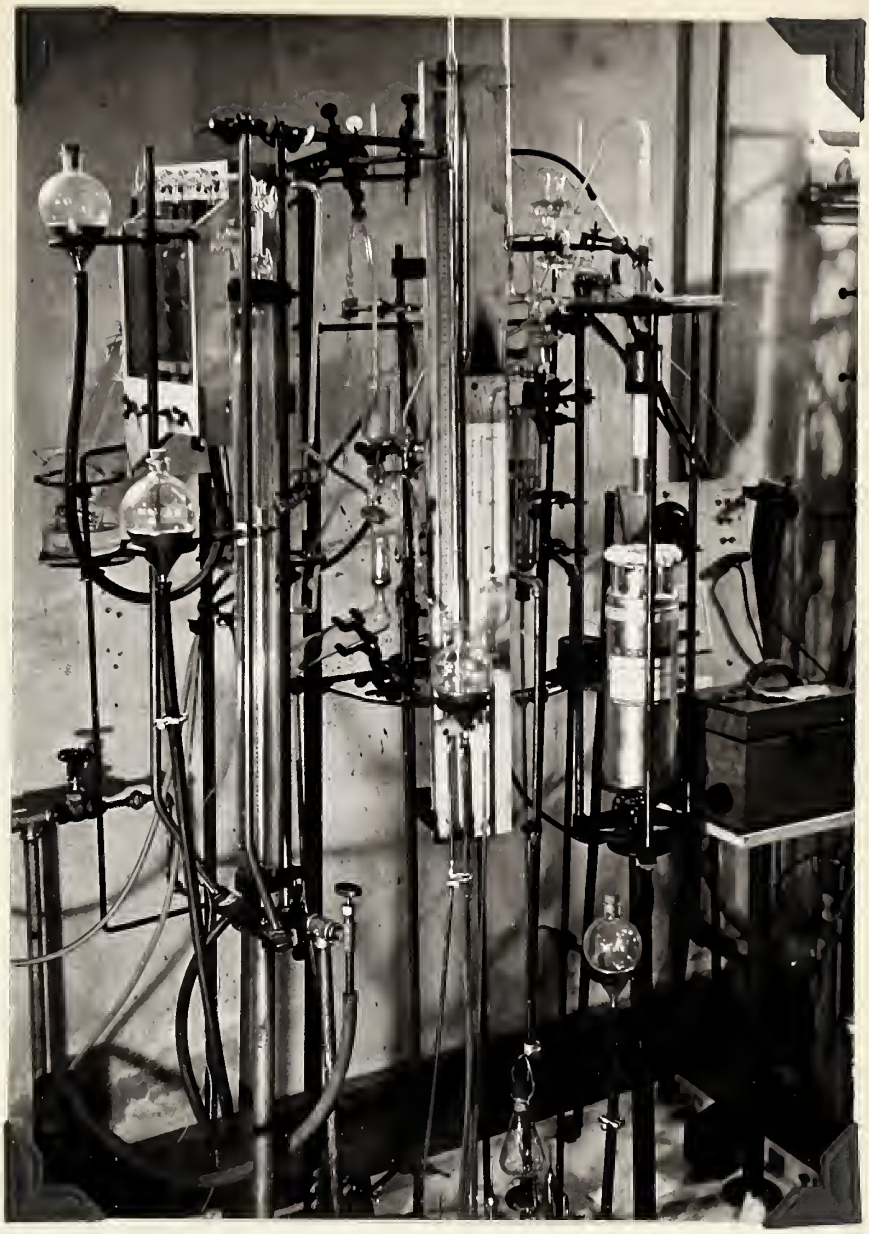


FIGURE 15 - The Portable Gas Analysis Apparatus.

Appendix I

Gas Analysis

Introduction

A new method of analysis of hydrocarbon gas mixtures, by fractional distillation at low temperatures, and low pressures has been fully described by Gillies and Hugill (8). The method was thoroughly tested by them. The best operating conditions for the fractionation column, were determined by analysis of known mixtures of hydrocarbon gases.

The analysis apparatus, as used by Gillies and Hugill, is a part of the main analytical apparatus, described previously in this thesis. Since this equipment embodies only one precision manometer and one Toepler pump, gas analyses, and pressure volume expansion measurements, may not be carried on at the same time.

In this appendix, a new portable, gas analysis apparatus will be described. Because of its compactness, and ease of operation, the new equipment presents a number of advantages, over the other apparatus.

A complete review of the literature, concerning low temperature fractionation, has been given by Gillies and Hugill, together with theoretical considerations. No further comments will be added here.

Description of Apparatus

A conventional drawing of the portable equipment is shown in Figure 16. The whole assembly is mounted on a wooden platform on casters, which enables it to be moved to any part of the laboratory. The apparatus may be levelled as a unit, by means of long bolts, through the platform.

The apparatus is essentially composed of two separate units, one for low temperature fractionations, and the other for combustion analyses. The sample of gas for combustion analysis may be taken directly from the Toepler pump P to the combustion analysis burette. This is an advantage over the original analysis apparatus. The Toepler pump is operated in a manner to keep vibration in the apparatus at a minimum. The mercury in the reservoir is displaced by water, under mains pressure. Combustion analyses were formerly carried out on a separate Improved Bureau of Mines Orsat apparatus.

Experience with the first fractionation column gave rise to improvements in the one made for the portable apparatus. The general design, as described by Gillies and Hugill, is unchanged. The column is about 1 inch shorter. Monel inlet and outlet tubes, are substituted for copper, to decrease the heat losses from the top of the column, to the atmosphere. It was found that only four thermocouples were necessary, to give a complete picture of the temperature gradient in the column. The middle thermocouple of the old column was dispens-

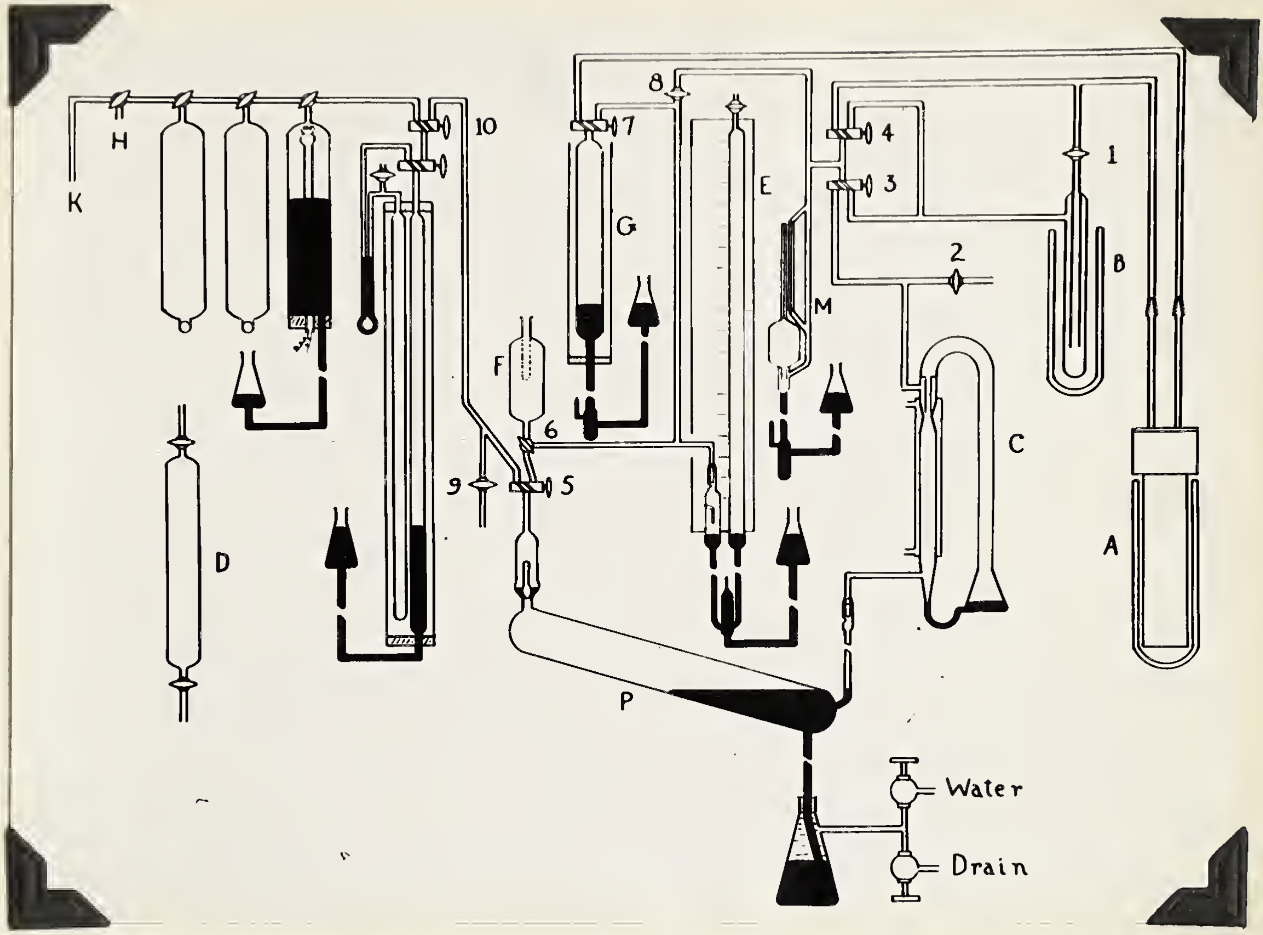


FIGURE 16 - Diagram of the Portable Gas Analysis Apparatus.

ed with. The column is supported by means of the Monel tubes, from a circular top plate of tempered Masonite, on which is mounted a terminal plate for the thermocouple and heater leads.

Operation.

Preliminary to carrying out an analysis, the whole fractionation unit (Figure 16) was evacuated by means of the Toepler pump P and the mercury diffusion pump C. With stopcock 10 closed, the gas was discharged to atmosphere through stopcocks 5 and 9. The fractionation column A and trap B were then isolated by closing stopcocks 1,3, and 4. Liquid air in Dewar flasks was brought up around the column and the trap. The level of the liquid air in the Dewar flask surrounding the column was approximately that of the top of the lower column heater. With stopcock 8 closed, the gas sample from the sample pipette, D, was admitted to the calibrated sample burette G, through the Toepler pump, the diffusion pump, and stopcocks 2,5,6 and 7. The mercury level in the sample burette was lowered to the calibration mark, by means of the levelling bulb. The pressure of the gas sample was measured by the constant volume manometer, E, and tap 7 was closed. By opening stopcocks 8 and 3, and reversing stopcock 5, the system was again evacuated. When the temperature gradient of the column had reached the required level, the gas was allowed to enter the column, slowly, from the sample burette. The gas

bubbled through a small slug of mercury in the line, which indicated the rate qualitatively. Experience showed that the gas must be admitted slowly to procure good fractionation in the column. Trap B, was opened to the McLeod gage through stopcock 4. Stopcock 1 was slightly opened to admit the methane fraction to the trap B. The pressure was equalized by slightly opening stopcock 3 to the diffusion pump and the Toepler pump. Stopcocks 1 and 3 were then fully opened, and the methane fraction pumped over into the fraction receiver F, through stopcocks 5 and 6, until the pressure in the trap was 1 mm. The diffusion pump was operated, until the pressure remained steady at 0.25 mm.

The amount of the methane fraction was measured by means of the constant volume manometer E. Stopcock 4 was then closed, and stopcock 5 opened, and the methane fraction pumped over to the burette of the combustion analysis apparatus through stopcock 10.

When the system was evacuated, stopcocks 3 and 8 were closed, and stopcock 5, reversed. The column was directly connected to the McLeod gage, by opening stopcock 4. Stopcock 1 was opened. The temperature along the fractionation column A was adjusted for ethane, and the ethane fraction allowed to distil over into the trap B. When the McLeod gage showed a pressure of 0.1 mm. or less, for three successive readings, with stopcock 1 closed, distillation was discontinued stopcock 4 was reversed, and stopcock 3 opened to the diffusion pump. The Dewar flask around the trap B was removed, and the ethane

fraction pumped over to the fraction receiver F, and measured by the manometer E.

The same procedure was repeated for each of the other constituents of the gas with the correct temperature distribution in the column. To take off the last fraction, pentanes, the column was warmed up to room temperature.

The amount of nitrogen in the methane fraction, was determined by the standard slow combustion method, using the combustion analysis unit. Oxygen from a cylinder was admitted at H. For the combustion analysis of the methane-nitrogen fraction from the older analytical apparatus, the sample was admitted at K from a sample tube D.

Discussion

The procedure described above, is essentially that used with the older analytical apparatus. The cutting temperatures and pressures are those which were used by Gillies and Hugill. Analyses were calculated on the basis of the sum of the volumes of all the fractions taken off. The volume per cent was obtained by dividing the volume of each component by the sum of the separate volumes.

With this new apparatus gas analyses may be done, while pressure-volume work is carried out on the main apparatus. Since the new apparatus is portable, it may be set up conveniently anywhere in the laboratory.

Summarizing the performance of this new equipment, the

time required for analysis is roughly 2½ hours. The liquid air consumption is roughly 3 lbs. for each analysis. The accuracy of the results is very good, duplicate analyses agreeint to within 0.1% for the major constituents methane, ethane, and to 0.03% for propane, butane and pentane.

BIBLIOGRAPHY

1. Boomer, E.H. and Johnson, C. A. - Unpublished paper

2. Davis, S.G, - Thesis 1940, University of Alberta Library

3. Deming, W.E. and Shupe L.E., - Phys. Rev. 37, 638, 1931

4. Deschner, W.W. and Brown, G.G. - I.E.C. 26, 836, 1940

5. van Dijck, W.J.D. - (To Shell Oil Co.), U.S. Patent 2, 201, 549, May 21, 1940

6. Edminster, W.C. - I.E.C. 28, 113, 1936

7. Ewell, R.H. - I.E.C. 32, 147, 1940

8. Gillies, A. and Hugill J.T. - Thesis 1940, University of Alberta Library

9. Gilliland, E.R. and Scheeline, H.W. - I.E.C. 32, 48, 1940

10 Henry, R.W. and Montgomery, J.V. - (To Phillips Petroleum Co.) U.S. Patent 2, 196, 989, April 16, 1940

11. Jessen, F.W. and Lightfoot, J.H. - I.E.C. 30, 312, 1938.

12. Johnson, C.A. - Thesis 1935, University of Alberta Library

13. Katz, D.L. and Hachmuth, K.H. - I.E.C. 29, 1072, 1937

14. Katz, D.L. and Kurata, F. - I.E.C. 32, 817, 1940

15. Kay, W.B. - I.E.C. 32, 353, 1940

16. Kvalnes, H.M. and Gaddy, V.L. - J.A.C.S. 53, 397, 1931

17. Lacey, W.N. - Am. Petroleum Inst. Bull. 210, 65, 1932.

18. Lewis, G.N. and Randall, M. - Thermodynamics and the Free Energy of Chemical Substances, New York, McGraw-Hill Book Co., 1923.

19. Maass, O. - J.A.C.S. 41, 53, 1919

20. Miller, H.C. - The Function of Natural Gas in the Production of Crude Oil, U.S. Bur. of Mines Report 1926

21. Nederbragt, G.W. - I.E.C. 30, 587, 1938

22. Petroleum and Natural Gas Conservation Board, Province of Alberta. Private Communication.

23. Piercey, A.G.A. - Thesis 1937, University of Alberta Library

24. Poynting, J.H. - Phil. Mag. 12, 32, 1881

25. Robinson, H.M. and Harding Bliss, - I.E.C. 32, 396, 1940

26. Sage, B.H. and Lacey, W.N. - I.E.C. 26, 652, 1934

27. Ibid. I.E.C. 28, 249, 1936

28. Ibid. I.E.C. 30, 1296, 1938

29. Ibid, I.E.C. 31, 1497, 1939

30. Sage, B.H. Lacey W.N. and Schaafsma, J.G. - I.E.C. 27, 49, 1935

31. Ibid. I.E.C. 26, 1218, 1934

32. Sage, B.H., Webster, D.C. and Lacey, W.N. - I.E.C. 29, 1192, 1937.

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